THE UNIVERSITY OF ALBERTA

CRITICAL SIZE OF BUBBLES IN LIQUID-GAS SOLUTIONS AT NEGATIVE PRESSURES

by

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

DEPARTMENT OF MECHANICAL ENGINEERING

EDMONTON, ALBERTA

SPRING, 1980

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

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Date . . Oct 30 1979 . . .

ABSTRACT

The equilibrium and stability of a gas-vapor bubble in a liquid-gas solution at negative pressures is investigated. The bubble is considered to exist at the center of rotation of a thin tube filled with the solution. The centrifugal field generated by the rotation of the system produces a state of tension in the solution surrounding the bubble.

The equilibrium shape of the bubble is shown to be approximated by a spheroid for which the plane section is an ellipse. However, for negative pressures in the solution the bubble is very close to being spherical. The stability analysis shows that the equilibrium state of the bubble is unstable, and the equilibrium size represents a critical value. A bubble less than the critical size will spontaneously collapse, while a bubble greater than the critical size will spontaneously grow.

Consideration is then restricted to a dilute, liquid-gas solution. The critical radius is expressed as a function of the properties of the liquid phase outside the center of the bubble. The dependence of the critical radius on the pressure, concentration, and temperature is investigated for the specific case of a dilute solution of air in water. The critical radius is found to decrease as the magnitude of the negative pressure increases. The presence of the dissolved

gas results in a small reduction in the critical radius at negative pressures.

ACKNOWLEDGEMENT

I wish to thank my supervisor, Dr. T. W. Forest, for the guidance and assistance he provided throughout the course of this work.

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LIST OF SYMBOLS

A	surface area
a	maximum radius of the gas-vapor bubble
B	eccentricity of an ellipse
b	half-length of the gas-vapor bubble
C	concentration of gas in a liquid
C_o	reference concentration of gas in a liquid
C_s	equilibrium concentration of gas in the liquid in the reference system
C_{so}	concentration of the solution at the membrane in the reference system
D	elemental quantity
D_c	diffusion coefficient
e	shape parameter
F	Helmholtz potential
f	dimensionless parameter
G	Gibb's potential
H_2	radius of curvature corresponding to the principal curvature κ_2
h	radius of curvature at the center of the gas-vapor bubble
I	moment of inertia of a body about a cylindrical axis
K	modulus of elliptic integral
K_H	Henry's law constant
k	Boltzmann's constant
ℓ	half-length of the centrifugal system

M_i	molecular weight of component i
m	mass
N_i	moles of component i
n	total number of components
$\hat{n}$	normal component of motion of the surface element DA
P	pressure
P_c^L	pressure in the liquid-gas solution at the center of the system
P_i	partial pressure of component i in the gas-vapor mixture
P_o	reference pressure for the centrifugal system
Pr	probability
P_r	general reference pressure
P_v	vapor pressure of the solvent
R	dimensionless radial co-ordinate
R_c	critical radius of a spherical gas-vapor bubble
r	radial co-ordinate
S	entropy
s	arc length of a curve
T	temperature
U	internal energy
V	volume
$\bar{V}_2$	partial molar volume of the solute in a solution
v^L	specific volume of the solvent
W_R	reversible work
X	dimensionless axial co-ordinate

X_i	mole fraction of component i
x	axial co-ordinate
Y	transformation variable
Z	transformation variable
Γ_i	adsorption of component i
γ	surface tension of the gas-vapor bubble
δ	virtual variation
ε	difference in the maximum radius between the equilibrium and non-equilibrium systems
η, η_1, η_2	dimensionless variables
Θ	angular co-ordinate
θ	angle associated with the slope of a curve
κ_1, κ_2	principal curvatures of the "dividing surface"
λ_i	undetermined multiplier
μ_i	chemical potential of component i
ξ_1, ξ_2	dimensionless variables
ρ	density
τ_D	characteristic time scale for diffusion
ϕ	angle between the normal to the curve and the positive x-axis
χ	angle between the normal and radial directions
Ψ	angle associated with elliptic integral
ψ	undetermined function of P and T
ω	angular velocity of the system

Subscripts

i	component i
j	component j
α	equilibrium state
β	non-equilibrium state
ν	equilibrium state without the gas-vapor bubble present

Superscripts

G	gas-vapor mixture
GR	gas-vapor mixture in the reference system
L	liquid-gas solution
LR	liquid-gas solution in the reference system
S	"dividing surface"
T	total quantity

CHAPTER 1

INTRODUCTION

The transition of a fluid from a liquid phase to a vapor phase characterizes many important fluid phenomena. Two of the most interesting of these from an engineering point of view are boiling and cavitation. Boiling and cavitation can be described as the explosive vaporization of the liquid into a vapor-filled cavity [1]. Boiling is caused by heating under constant pressure, while cavitation is the result of a reduction in pressure at essentially constant temperature. The onset of both of these phase transition phenomena is not as yet fully understood. For example, cavitation is said to occur when the pressure in the fluid drops below the vapor pressure of the liquid. In actual practice, this criterion is much too simple to be able to accurately predict the onset of cavitation.

Boiling and cavitation represent phase transitions as a result of a metastable state in a liquid. A metastable state is stable for infinitesimal deviations about the equilibrium state; however, for a finite deviation, the system does not return to the original state, but proceeds to some other equilibrium state for which the entropy of the system is greater than in the original state. Given enough time, a system will move from a metastable state to a stable one.

The mechanism of this phase transition is crucial to an understanding of boiling and cavitation.

Both boiling and cavitation require the formation of a vapor cavity of particular size in the metastable liquid state. According to Plesset [2],"a central problem in cavitation and boiling is how macroscopic vapor cavities can form when moderate tensions are applied to a liquid". If the liquid pressure is mechanically reduced sufficiently below the vapor pressure, the liquid can enter a state of tension, or negative pressure. Negative pressures are made possible in a liquid by intermolecular attraction. In this sense, a liquid more closely resembles an amorphous solid than a gas.

Theoretical calculations have shown that the fracture of a pure liquid leading to the creation of a vapor cavity could only be produced by extremely large tensions[1] or superheats [4]. However, experimentally much lower tensile strengths and superheat limits have been obtained for common engineering fluids. In an attempt to explain the relatively low tensions and superheats commonly encountered, the presence of nuclei has been postulated in ordinary liquids. These nuclei would serve to initiate the formation of the vapor cavity.

It is well known that a "dirty" liquid has a much lower tensile strength than the pure liquid. Heterogeneous

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[1]For water at 300°K, Fischer [3] calculated a tensile limit of approximately 134 MPa.

nucleation theory considers a foreign particle or surface to serve as the nucleation site. Thus, the presence of a surface or colloidal impurity in the liquid would be responsible for the reduction in tensile strength.

Another possible reason for the low liquid tensions experimentally obtained is the presence of dissolved gas. Even when careful attention is given to the purity of the liquid, in practice small amounts of dissolved gas are usually present. To date, the effect of the presence of dissolved gas on the tensile strength of a liquid has not been conclusively determined. There is general disagreement as to whether the gas significantly lowers the tensile limit [5].

The presence of dissolved gas is important when the vapor cavity formation is initiated by homogeneous bubble nucleation. Homogeneous nucleation theory [6,7] postulates that a thermodynamic fluctuation in a metastable state produces an "embryo" of the new phase, which if sufficiently large in size serves to initiate the phase transition. For the transition of a liquid to a vapor, the embryo can be regarded as a very small vapor bubble or nucleus. From statistical physics [8], it is understood that the instantaneous value of the density of a liquid fluctuates over a range of values. Figure 1-1 illustrates the density at a particular location in a liquid as a function of time. Although the instantaneous value fluctuates rapidly, the

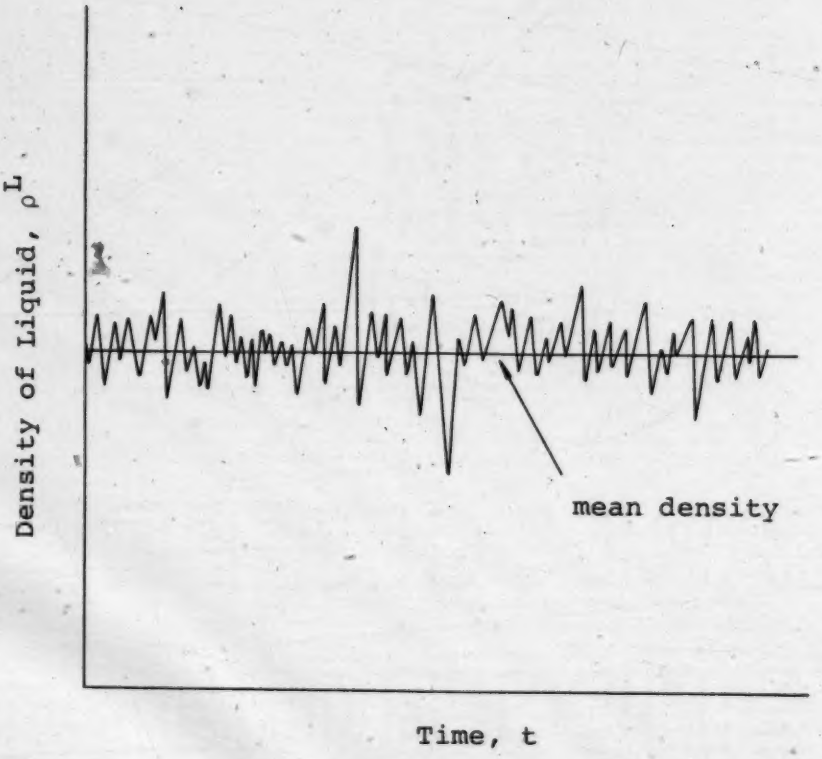

Figure 1-1 Density Fluctuations in a Liquid with Time

time average value remains constant for a stable equilibrium state. Small deviations in the density do not disturb the equilibrium state of the liquid. However, a sufficiently large fluctuation in the density of the liquid can cause a vapor nucleus to be formed. For a liquid phase in a metastable state, it is possible that the nucleus will not decay as it does for a stable equilibrium state, but instead grow to form a center for vaporization.

Whether the nucleus grows or decays is explained by the concept of a critical size, or in the case of a spherical nucleus, a critical radius. There is a critical size for which a nucleus in a metastable state will grow to become a center for the formation of a new phase. If the nucleus is less than the critical size, the nucleus will decay. However, if the nucleus is greater than the critical size, the nucleus will grow to become in this case a center for vaporization.

From statistical physics [9], it is possible to predict the probability that a critical size nucleus will occur. The probability, Pr, is inversely proportional to the exponential of the reversible work, W_R, required to form the nucleus, i.e.

$$Pr \propto \exp\left(-\frac{W_R}{kT}\right) \qquad (1\text{-}1)$$

where k is Boltzmann's constant, and T is the temperature. The reversible work in the above expression is a function of

the critical size of the vapor nucleus.

Although the discussion has referred so far to a pure liquid, it is of special interest to consider the case of a liquid-gas solution in order to include the effect of the dissolved gas on the system. The reversible work required to form a critical size nucleus in a liquid-gas solution can be determined if the size of the nucleus has been obtained as a function of the properties of the solution. For a spherical nucleus of radius R_c, in a two component solution, a useful representation is

$$R_c = R_c\,(T,P,C) \qquad (1\text{-}2)$$

where T, P, and C are, respectively, the temperature, pressure, and concentration of the solution.

Ward, Balakrishnan, and Hooper [10] have developed an expression for the critical radius of a gas-vapor bubble in a liquid-gas solution at positive pressure. The conditions of thermodynamic equilibrium for the general case of a multicomponent solution yielded the equality of chemical potentials, and the Laplace equation of capillarity relating the pressure difference across the interface to the curvature of the bubble at that point. For the special case of a dilute solution of a gas in a liquid, the critical radius of a spherical bubble was expressed as a function of the temperature, concentration, and pressure of the dilute

solution,[2] i.e.

$$R_c = \frac{2\gamma}{\eta P_v + P\frac{C}{C_o} - P} \qquad (1\text{-}2)$$

where

$$\eta \equiv \exp\left[\frac{v^L}{kT}(P-P_v) - C\right] \qquad (1\text{-}3)$$

The surface tension γ, specific volume v^L, and vapor pressure P_v are functions of the temperature, T. The reference concentration C_o is that of the liquid saturated with the gas across a flat, non-rigid membrane permeable only to the gas component. The reference system is strictly limited to positive pressures for the liquid. If the liquid is in a state of tension, the equality of pressure across the membrane would require the gas to also exist at a negative pressure, which is impossible. Thus, the expression for the critical radius given by equation (1-2) is only valid for positive pressures in the solution.

If homogeneous nucleation theory is to be used to explain the onset of cavitation and boiling in liquid-gas solutions, the expression for the critical size of a gas-vapor nucleus must be extended to include the possibility of negative pressures. From this expression, the reversible work required to form a critical size nucleus in such a metastable

---

[2] Since Ward et al. included the effect of non-ideal gas behavior inside the bubble, the expression obtained for R_c included the activity coefficients of each component. Expression (1-2) results from setting the activity coefficients equal to one in the original expression, i.e. it is assumed that the gas and vapor inside the bubble behave as an ideal gas mixture.

state can be calculated. Once the reversible work is known, the probability of the formation of a critical size nucleus can be obtained. This investigation will consider an expression for the critical size of a gas-vapor nucleus in a liquid-gas solution at negative pressure, and relate it to the reversible work required to form the nucleus.

Since this investigation will involve a solution at negative pressure, it is useful to consider some of the techniques that have been developed for producing tensions in liquids. The principal purpose of experimentally generating negative pressures in liquids has been the measurement of liquid tensile strengths. A thorough review of the methods used to determine the tensile strengths of liquids, and some of the results obtained are given by Blake [11].

One method of generating liquid tensions is by the use of pressure fields. For example, the region of rarefaction for an acoustical standing wave in a liquid can exhibit negative pressures. Galloway [12] used this technique to study sonically induced cavitation in water and benzene, among other liquids. Radially symmetric standing waves produced by a spherical resonator were used to generate acoustic pressures in the body of the liquid away from any solid surface. Dynamic tensile strengths of approximately 20 MPa for water and 14 MPa for benzene were obtained. It was determined that the air content of the liquid significantly limited the maximum negative pressure the liquid could

withstand. Figure 1-2 illustrates Galloway's results for the dependence of the cavitation threshold pressure of water and benzene on the percentage air concentration.

A centrifugal pressure field can also be used to generate liquid tensions. A description of the method used by Briggs [13] will suffice to explain the technique involved. The liquid was contained in a thin capillary tube open at both ends. About one centimeter from each end, the tube was bent back upon itself through an angle of 140° to form a Z shape. The tube was mounted on a spinner connected to the end of a vertical shaft of an electric motor. The entire system was enclosed in a large cylinder. When operating, the air pressure inside the cylinder was reduced to 4 or 5 kPa (3 or 4 cm Hg). The tube was mounted on a horizontal plane with the center intersecting the projected spin axis. Thus, when spinning, each half column of liquid pulled against the other, placing the liquid at the center in a state of tension. The fracture of the column of liquid at the mid-point of the tube indicated that the maximum tensile strength had been reached. Knowledge of the length of the tube and the angular velocity of the system enabled the maximum negative pressure to be calculated for a liquid of given density. Briggs notes that "scrupulous cleanliness" was necessary.

Reynolds [14], in 1878, was the first to use a centrifugal system to measure the tensile strength of a liquid.

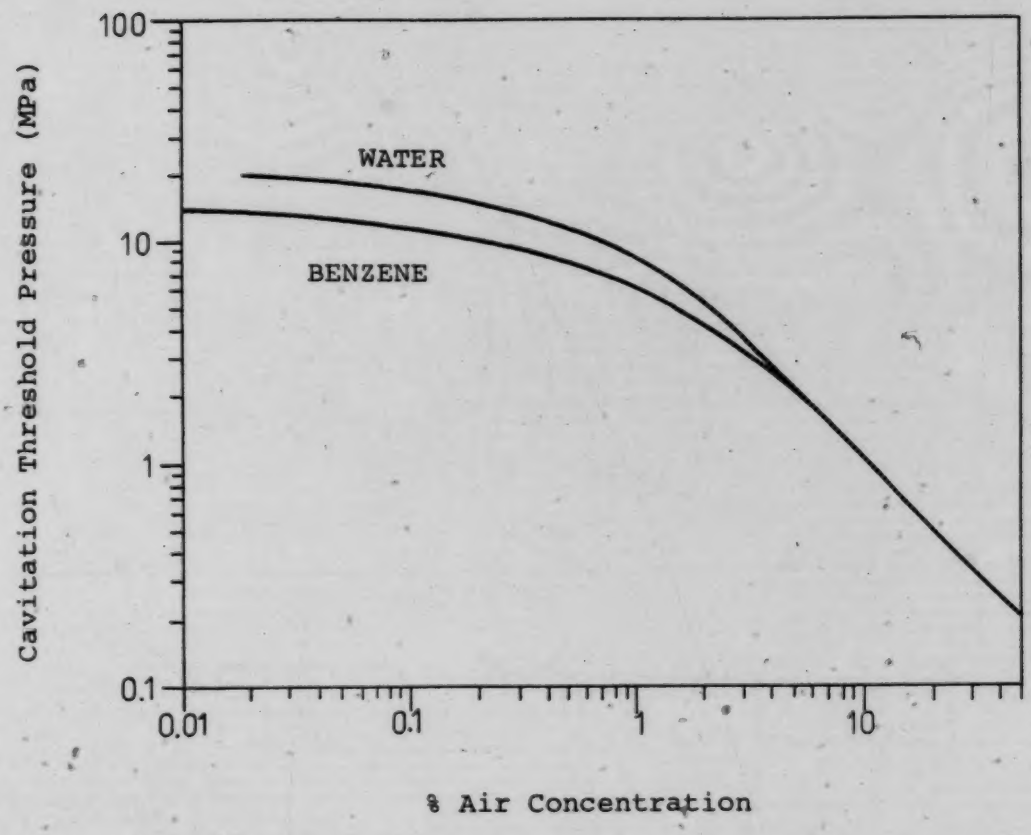

Figure 1-2 Galloway's Experimental Results for the Dependence of the Cavitation Threshold Pressure on the Percentage Gas Concentration. (100% corresponds to the saturation concentration at a pressure of 0.10 MPa and a temperature of 22°C)

He obtained a maximum tension of about 0.49 MPa for ordinary tap water. Temperley and Chambers [15], in an attempt to repeat his results in 1946, obtained a maximum value of 0.57 MPa for water at room temperature. The largest experimentally measured tension for water is that due to Briggs. Using the centrifugal system described above, he obtained a maximum tension of about 27.7 MPa for water around 10°C.

A centrifugal system has also been applied to the study of liquids other than water. Apfel and Smith [16] obtained a maximum tension of 17.6 MPa for di-ethyl ether using an air-driven centrifugal device. The significance of this value is that it lies "between 88 and 93 per cent of the tensile strength of di-ethyl ether at room temperature as predicted by homogeneous nucleation theory." Donoghue, Vollrath, and Gerjuoy [17] obtained a maximum tension of 15.9 MPa for benzene using a system similar to that of Briggs. Like Galloway, Donoghue et al. observed the effect of dissolved gas on the tensile strength of benzene. Some of their results are presented in Figure 1-3. They indicate that the rupture strength is decreased by the addition of dissolved gas.

Although the results of Galloway and Donoghue et al. suggest that the presence of dissolved gas decreases the tensile strength of a liquid, their results are not conclusive. In a brief discussion of Galloway's results, Hammitt [18] notes that for a higher gas content, i.e. fifty to

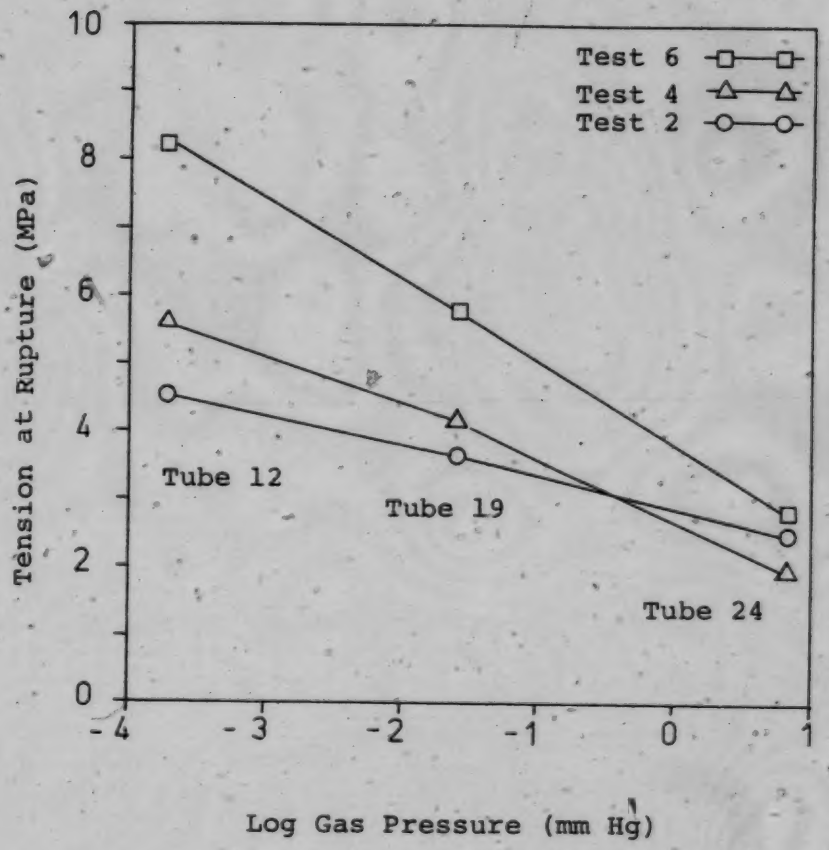

Figure 1-3 Results of Donoghue et al. for the Dependence of the Rupture Strength of Benzene on the Dissolved Gas Content

ninety-five per cent saturation, the results of Iyengar and Richardson [19] using ultrasonic cavitation in static systems show no effect of dissolved air on the cavitation threshold. Kuper and Trevena [20] reported on theoretical grounds that "the presence of dissolved gas only causes a negligible diminution in the intrinsic strength of liquids." Harvey [21] found that prepressurizing the liquid to drive the free gas into solution enabled considerable tensions to be obtained in water. He demonstrated that in considering the effect of gas content on the tensile strength of liquids, one must discriminate between dissolved and undissolved gas.

In general, it should be noted that the use of a centrifugal system to measure the tensile strength of a liquid requires that the rupture originate in the body of the liquid. However, in many cases it has not been clearly established whether the liquid column fails due to loss of adhesion at the walls of the tube or loss of cohesion in the body of the liquid.

This investigation will consider the use of a centrifugal field to produce a region of negative pressure in a liquid. If a gas-vapor nucleus is imagined to exist at the center of rotation of a system similar to that of Briggs, the solution outside the nucleus would be subject to negative pressures. Thus, the thermodynamic analysis of a gas-vapor nucleus located at the axis of rotation of a narrow tube filled with a liquid-gas solution will yield an expression

for the critical size similar to that obtained by Ward et al., valid for the case of negative pressure. The expression for the critical size of the nucleus in terms of the properties of the solution will require the use of a special reference system different from that of Ward et al., which is valid for a solution at negative pressure.

For a system subject to a centrifugal field, the deformation of the bubble must be considered. A gas-vapor bubble rotating about a central axis cannot be assumed to have a spherical shape. Rather, the effect of the centrifugal field would be such as to produce a deformation consistent with the axial symmetry of the system. Lord Rayleigh [22] considered the effect of "capillary tension" on an incompressible fluid mass rotating with uniform angular velocity. He solved the differential equation for the system using a power series expansion. When only first order terms were considered, the shape of a plane section through the axis of rotation of the bubble was approximated by an ellipse.

Rosenthal [23] and Princen, Zia, and Mason [24] both considered the shape of a fluid bubble immersed in and rotating with a heavier fluid. Beginning with Laplace's equation of capillarity, both obtained solutions for the shape of a plane section through the axis of rotation in terms of elliptic integrals of the first and second kind. Each method differed in the choice of the bubble parameter to which the size and shape were referenced, although the results were

easily related. Both concluded that for high angular velocities, the shape of the bubble became essentially that of a cylinder with rounded ends.

Princen et al. used their expression for the bubble length to determine the interfacial tension of an experimental system. Measuring the length of a bubble of known volume at a given speed enabled them to calculate the surface tension. In the course of their experiments, they observed the bubble to become cylindrical in shape for large angular velocities, as they had predicted.

The conclusions of Rosenthal and Princen et al. are not directly applicable since their systems treated fluid bubbles of constant volume. That is, a bubble of given volume initially placed in their systems at rest, will retain that volume even when accelerated to different angular velocities. For a gas-vapor bubble in a liquid-gas solution, the effect of mass transfer across the interface must be included. The equilibrium conditions will determine the distribution of mass inside and outside the bubble.

In this investigation, the conditions of thermodynamic equilibrium will be obtained for a gas-vapor nucleus at the center of rotation of a centrifugal system. A stability analysis will determine the nature of the equilibrium state. From the conditions of equilibrium, the shape of the bubble will be obtained for negative pressures in the solution outside the bubble. For the specific case of a gas-vapor bubble

in a dilute solution, the use of an appropriate reference condition will enable the critical size to be expressed in terms of the properties of the dilute solution.

CHAPTER 2

THE EQUILIBRIUM STATE OF A GAS-VAPOR BUBBLE IN A LIQUID-GAS SOLUTION SUBJECT TO A CENTRIFUGAL FIELD

2.1 The Equilibrium Conditions

This section considers the conditions of thermodynamic equilibrium for a gas-vapor bubble in a multicomponent liquid-gas solution at negative pressure. In order to place the liquid phase outside the bubble in a state of tension, the entire system is considered subject to a centrifugal field.

The thermodynamic system is represented by the schematic in Figure 2.1-1. A long, narrow tube rotates at constant velocity around a central axis denoted x. The tube is filled with a solution of n-1 gases in an incompressible liquid. Each chemical component is considered to be inert, i.e. there are no chemical reactions in the system. The pressure in the liquid solution at both ends of the tube--a radial distance ℓ from the x-axis--is denoted by the reference pressure P_o. A single gas-vapor bubble is located at the center of the tube in the liquid-gas solution. The liquid-gas solution containing the gas-vapor bubble composes the thermodynamic system considered. The entire system is assumed to rotate with angular velocity ω, and there are no other

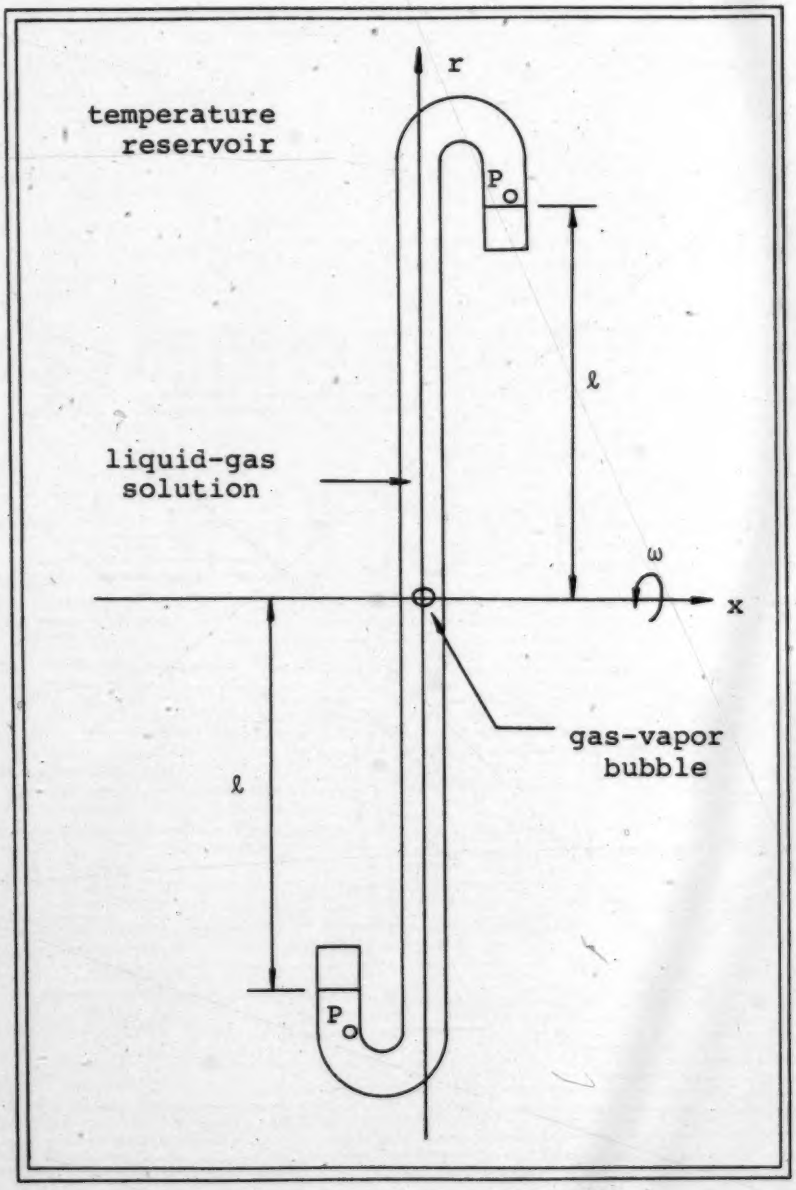

Figure 2.1-1 The Thermodynamic System

fields acting on the system. For the closed, constant-volume system considered, the total mass and total volume remain constant. The entire system is in diathermal contact with a heat reservoir at temperature T.

The equilibrium state of a thermodynamic system is that which minimizes the value of the internal energy for a fixed value of the total entropy. However, for a system at constant temperature, it is more convenient to use the Helmholtz potential.[1] The natural variables for the Helmholtz potential, F, are the temperature, T, volume, V, and mole numbers, $\underset{\sim}{N}$.[2] The equilibrium state for a system at constant temperature is that which minimizes the value of the Helmholtz potential at that temperature [25]. The advantage of using the Helmholtz potential formulation is a reduction by one in the number of independent variables due to the constant temperature condition. Given an expression for the total free energy of the system, the equilibrium conditions are obtained by setting the variation of the energy at constant temperature equal to zero.

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[1]The Helmholtz potential is the Legendre transformation of the internal energy, U, replacing the entropy, S, by the temperature, T, as an independent variable, i.e.

$$F = U - TS$$

[2]The number of molecules, expressed in moles, of a chemical component i is denoted by the mole number N_i. The notation $\underset{\sim}{N}$ is used to represent the mole numbers of each of the respective components, i.e.

$$N_1, N_2, \ldots, N_n.$$

The first step in the equilibrium analysis is to formulate an expression for the total free energy of the system using the Helmholtz potential representation. The total system represented in Figure 2.1-1 is comprised of three subsystems: the liquid-gas solution, the gas-vapor mixture, and the interface, denoted by the superscripts L, G, and S, respectively. Figure 2.1-2 illustrates the three subsystems created by the bubble surface. The properties of a single subsystem are not uniform and homogeneous throughout due to the influence of the centrifugal field. In order to account for the spatial variation of the local properties, small elements of each subsystem are considered. The symbol D is used to indicate small quantities of the extensive variables[3] for which the properties are constant.

The Helmholtz potential in the liquid-gas solution and the gas-vapor mixture can be expressed as a function of the local values of the temperature, volume, and mole numbers of the chemical components. The expression for the Helmholtz potential of a small element of either subsystem at constant temperature is

$$DF = - PDV + \sum_{i=1}^{n} \mu_i DN_i \qquad (2.1\text{-}1)$$

where P is the pressure, and μ_i is the chemical potential of the ith component. Equation (2.1-1) can be integrated over each subsystem to obtain an expression for the Helmholtz

[3] An extensive variable or parameter is one that is additive over the extent of the system, i.e. V or N_i.

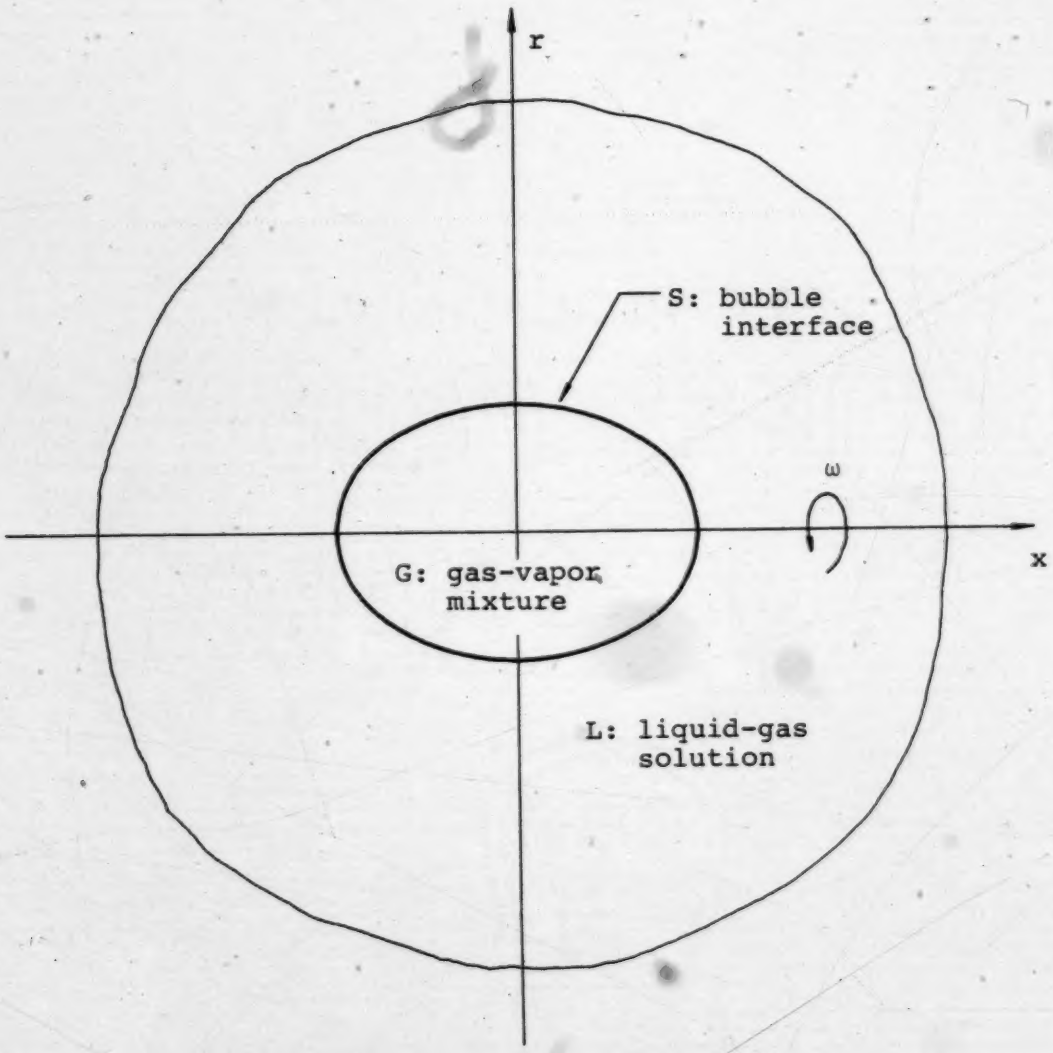

Figure 2.1-2 The Three Major Subsystems

potential of the liquid-gas solution and the gas-vapor mixture, i.e.

$$F^L = \int_{V^L} - P^L DV^L + \sum_{i=1}^{n} \int_{N_i^L} \mu_i^L \, DN_i^L \qquad (2.1\text{-}2)$$

and

$$F^G = \int_{V^G} - P^G DV^G + \sum_{i=1}^{n} \int_{N_i^G} \mu_i^G \, DN_i^G \qquad (2.1\text{-}3)$$

The expression for the Helmholtz potential associated with the interface is obtained from surface thermodynamics [26]. The interface is modelled as a mathematical surface of discontinuity called the "dividing surface". The position of the "dividing surface" is so chosen as to eliminate the dependence of the free energy associated with the interface on the curvature of the surface [27]. It has zero thickness, and hence no volume. The area replaces the volume as an independent parameter in the expression for the Helmholtz potential. Excess quantities[4] are associated with the "dividing surface" in an analogous way to their counterparts in the other two systems. Thus, the Helmholtz potential in the interface is expressed as a function of the temperature, area, and excess mole numbers of the chemical components.

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[4] An excess quantity represents the difference between the actual amount of an extensive quantity contained in the interfacial region, and the amount that would be contained if the phases on either side of the "dividing surface" were assumed to extend right up to the surface in a continuous and uniform manner.

The expression for the Helmholtz potential of a small element, DA, of the "dividing surface" at constant temperature is

$$DF^S = \gamma DA + \sum_{i=1}^{n} \mu_i^S \, DN_i^S \qquad (2.1\text{-}4)$$

where γ is the surface tension [28]. Integrating over the "dividing surface" gives the expression for the Helmholtz potential of the interface, i.e.

$$F^S = \int_A \gamma DA + \sum_{i=1}^{n} \int_{N_i^S} \mu_i^S \, DN_i^S \qquad (2.1\text{-}5)$$

The Helmholtz potential of the entire system is simply the sum of the potentials of the three subsystems, i.e.

$$F = F^L + F^G + F^S \qquad (2.1\text{-}6)$$

Using equations (2.1-2), (2.1-3), and (2.1-5) in (2.1-6) gives an expression for the intrinsic free energy of the total system, i.e.

$$F = \int_{V^L} - P^L DV^L + \sum_{i=1}^{n} \int_{N_i^L} \mu_i^L \, DN_i^L +$$

$$+ \int_{V^G} - P^G DV^G + \sum_{i=1}^{n} \int_{N_i^G} \mu_i^G \, DN_i^G +$$

$$+ \int_{A} \gamma DA + \sum_{i=1}^{n} \int_{N_i^S} \mu_i^S \, DN_i^S \qquad (2.1\text{-}7)$$

The system shown in Figure 2.1-1 is subject to a centrifugal field generated by a rotation about the central axis. The expression for the intrinsic free energy given by equation (2.1-7) does not include the energy contribution due to the field. The potential energy associated with a small element of mass, Dm, in the presence of the field is

$$-\frac{1}{2} \omega^2 r^2 \, Dm \qquad (2.1\text{-}8)$$

where ω is the angular velocity, and r is the radial distance of element Dm from the axis of rotation.[5]

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[5]The method whereby the effect of the centrifugal field is introduced closely follows that developed by Gibbs [29] in treating the equilibrium of a system under the influence of gravity.

Integrating expression (2.1-8) over each subsystem gives the contribution of the centrifugal field to the free energy of each subsystem, i.e.

$$\int_m -\frac{1}{2}\,\omega^2 r^2\,Dm \tag{2.1-9}$$

Finally, combining expressions (2.1-7) and (2.1-9) yields an expression for the total free energy, F, of the system including the effect of the centrifugal field, i.e.

$$F = \int_{V^L} -P^L DV^L + \sum_{i=1}^{n} \int_{N_i^L} \mu_i^L DN_i^L + \int_{m^L} -\frac{1}{2}\,\omega^2 r^2 Dm^L$$

$$+ \int_{V^G} -P^G DV^G + \sum_{i=1}^{n} \int_{N_i^G} \mu_i^G DN_i^G + \int_{m^G} -\frac{1}{2}\,\omega^2 r^2 Dm^G$$

$$+ \int_A \gamma DA + \sum_{i=1}^{n} \int_{N_i^S} \mu_i^S DN_i^S + \int_{m^S} -\frac{1}{2}\,\omega^2 r^2 Dm^S \tag{2.1-10}$$

The condition for an extremum of the free energy can be expressed as

$$\delta F \Big|_{T,V,\underset{\sim}{N}} = 0 \qquad (2.1\text{-}11)$$

The δ notation is used to indicate a virtual variation of the Helmholtz potential. The variation in equation (2.1-11) is subject to the following constraints:

$$T = \text{constant} \qquad (2.1\text{-}12)$$

$$\int_{V^L} DV^L + \int_{V^G} DV^G = V^T \qquad (2.1\text{-}13)$$

$$\int_{N_i^L} DN_i^L + \int_{N_i^G} DN_i^G + \int_{N_i^S} DN_i^S = N_i^T, \quad i=1,2,\ldots,n \qquad (2.1\text{-}14)$$

where V^T and N_i^T represent the total volume and total mole numbers of the entire system. For the closed, constant-volume system considered, V^T and N_i^T in the above equations are constant. Using expression (2.1-10), the variation of the free energy in equation (2.1-11) can be expressed as

$$\delta F = \int_{V^L} - P^L \delta DV^L + \sum_{i=1}^{n} \int_{N_i^L} \mu_i{}^L \delta DN_i{}^L + \int_{m^L} - \frac{1}{2} \omega^2 \delta (r^2 Dm^L)$$

$$+ \int_{V^G} - P^G \delta DV^G + \sum_{i=1}^{n} \int_{N_i^G} \mu_i{}^G \delta DN_i{}^G + \int_{m^G} - \frac{1}{2} \omega^2 \delta (r^2 Dm^G)$$

$$+ \int_{A} \gamma \, \delta DA + \sum_{i=1}^{n} \int_{N_i^S} \mu_i{}^S \delta DN_i{}^S + \int_{m^S} - \frac{1}{2} \omega^2 \delta (r^2 Dm^S) \qquad (2.1\text{-}15)$$

In general

$$\delta(r^2 Dm) = 2r\delta r \, Dm + r^2 \delta Dm \qquad (2.1\text{-}16)$$

For the liquid-gas solution and the gas-vapor mixture, the element of mass Dm can be expressed as ρDV or $\sum_{i=1}^{n} M_i DN_i$, where ρ is the density and M_i is the molecular weight of component i. Then equation (2.1-16) becomes

$$\delta(r^2 Dm) = 2r\delta r \rho DV + \sum_{i=1}^{n} r^2 M_i \, \delta DN_i \qquad (2.1\text{-}17)$$

Likewise, for the interface, the element of mass Dm can be expressed as ΓDA or $\sum_{i=1}^{n} M_i DN_i{}^S$. The symbol Γ_i denotes the

adsorption[6] of component i at the interface, defined by

$$\Gamma_i = \frac{N_i^S}{A} \tag{2.1-18}$$

The total adsorption is the sum of the individual quantities, i.e.

$$\Gamma = \sum_{i=1}^{n} \Gamma_i \tag{2.1-19}$$

For the interface, equation (2.1-16) becomes

$$\delta(r^2 Dm) = 2r\delta r\, \Gamma DA + \sum_{i=1}^{n} r^2 M_i\, \delta N_i^S \tag{2.1-20}$$

Using expressions (2.1-15), (2.1-17), and (2.1-20) in equation (2.1-11) yields an expression for the extremum condition in terms of the thermodynamic variables of the system, i.e.

$$\int_{V^L} - P^L\, \delta DV^L + \int_{V^L} - \omega^2 r\, \delta r \rho^L DV^L + \sum_{i=1}^{n} \int_{N_i^L} (\mu_i^L - \tfrac{1}{2}\omega^2 r^2 M_i)\, \delta DN_i^L$$

$$+ \int_{V^G} - P^G \delta DV^G + \int_{V^G} - \omega^2 r \delta r \rho^G DV^G + \sum_{i=1}^{n} \int_{N_i^G} (\mu_i^G - \tfrac{1}{2}\omega^2 r^2 M_i)\, \delta DN_i^G$$

$$+ \int_A \gamma \delta DA + \int_A - \omega^2 r \delta r \Gamma DA + \sum_{i=1}^{n} \int_{N_i^S} (\mu_i^S - \tfrac{1}{2}\omega^2 r^2 M_i)\, \delta DN_i^S = 0 \tag{2.1-21}$$

[6] An alternate name for the adsorption is the superficial density.

The equilibrium conditions are obtained from equation (2.1-21) subject to the constraints given by equations (2.1-12), (2.1-13), and (2.1-14). Since variations in the volume and surface area are independent of variations in the mole numbers, equation (2.1-21) can be expressed as two separate conditions, i.e.

$$\int_{V^L} - P^L \, \delta DV^L + \int_{V^L} - \omega^2 r \, \delta r\rho^L \, DV^L + \int_{V^G} - P^G \, \delta DV^G$$

$$+ \int_{V^G} - \omega^2 r \delta r \rho^G \, DV^G + \int_A \gamma \delta DA + \int_A - \omega^2 r \delta r \, \Gamma \, DA = 0 \qquad (2.1\text{-}22)$$

and

$$\sum_{i=1}^{n} \int_{N_i^L} (\mu_i^L - \tfrac{1}{2} \omega^2 r^2) \, \delta DN_i^L + \sum_{i=1}^{n} \int_{N_i^G} (\mu_i^G - \tfrac{1}{2} \omega^2 r^2) \, \delta DN_i^G$$

$$+ \sum_{i=1}^{n} \int_{N_i^S} (\mu_i^S - \tfrac{1}{2} \omega^2 r^2) \, \delta DN_i^S = 0 \qquad (2.1\text{-}23)$$

The conditions of constraint given by equations (2.1-13) and (2.1-14) expressed in terms of variations in volume and mole numbers become

$$\int_{V^L} \delta DV^L + \int_{V^G} \delta DV^G = 0 \qquad (2.1\text{-}24)$$

$$\int_{N_i^L} \delta DN_i^L + \int_{N_i^G} \delta DN_i^G + \int_{N_i^S} \delta DN_i^S = 0, \quad i=1,2,\ldots,n \qquad (2.1\text{-}25)$$

Equation (2.1-22) represents the condition of mechanical equilibrium. The variation of the system is expressed as variations in the size and position of the volume and surface elements. Considering the pressure-volume terms first, by simple differentiation

$$\int_V P\delta DV = \delta \int_V PDV - \int_V \delta PDV \qquad (2.1\text{-}26)$$

In the equation above, δP represents the variation in the pressure associated with the change in position of the volume element DV. For a volume, V, bounded by a surface, A,

$$\delta \int_V PDV = \int_A P\, \delta\hat{n}\, DA \qquad (2.1\text{-}27)$$

where $\delta\hat{n}$ is the normal component of the motion of DA, positive when outward with respect to V. Using equation (2.1-27) in (2.1-26) gives

$$\int_V P\,\delta DV = \int_A P\delta\hat{n}\,DA - \int_V \delta P DV \qquad (2.1\text{-}28)$$

In terms of the liquid-gas solution, V^L, and the gas-vapor mixture, V^G, equation (2.1-28) becomes

$$\int_{V^L} P^L\,\delta DV^L + \int_{V^G} P^G\,\delta DV^G = \int_A (P^G - P^L)_A\,\delta\hat{n}\,DA$$

$$- \int_{V^L} \delta P^L\,DV^L - \int_{V^G} \delta P^G\,DV^G \qquad (2.1\text{-}29)$$

where $(P^G - P^L)_A$ is the pressure difference across the surface element DA, and $\delta\hat{n}$ is positive when projecting outward from V^G into V^L.

Consider now the surface terms in equation (2.1-22). Again, differentiating gives

$$\int_A \gamma\delta DA = \delta \int_A \gamma DA - \int_A \delta\gamma DA \qquad (2.1\text{-}30)$$

where $\delta\gamma$ is the variation in the surface tension associated with the component of motion of the surface element DA lying in the surface. For the "dividing surface", A, with principal curvatures κ_1 and κ_2,

$$\delta \int_A \gamma DA = \int_A \gamma(\kappa_1 + \kappa_2)\, \delta\hat{n}\, DA \qquad (2.1\text{-}31)$$

where the curvatures are considered positive when the centers are inside V^G. Using equation (2.1-31) in (2.1-30) gives

$$\int_A \gamma\delta DA = \int_A \gamma(\kappa_1 + \kappa_2)\, \delta\hat{n}\, DA - \int_A \delta\gamma DA \qquad (2.1\text{-}32)$$

Finally, by means of equations (2.1-29) and (2.1-32), the general condition of mechanical equilibrium is reduced to

$$\int_{V^L} (\delta P^L - \rho^L \omega^2 r \delta r)\, DV^L + \int_{V^G} (\delta P^G - \rho^G \omega^2 r \delta r)\, DV^G$$

$$+ \int_A [-(P^G - P^L)_A\, \delta\hat{n} + \gamma(\kappa_1 + \kappa_2)\delta\hat{n} - \Gamma\omega^2 r\delta r - \delta\gamma]\, DA = 0 \qquad (2.1\text{-}33)$$

Equation (2.1-33) is satisfied by the condition that the integrands vanish throughout the system, i.e.

$$\frac{dP^L}{dr} = \rho^L \omega^2 r \tag{2.1-34}$$

$$\frac{dP^G}{dr} = \rho^G \omega^2 r \tag{2.1-35}$$

$$-(P^G - P^L)_A \, \delta\hat{n} + \gamma \, (\kappa_1 + \kappa_2) \, \delta\hat{n} - \Gamma \, \omega^2 r \delta r - \delta\gamma = 0 \tag{2.1-36}$$

Separating the variations in equation (2.1-36) into normal and tangential motions of DA yields

$$(P^G - P^L)_A = \gamma \, (\kappa_1 + \kappa_2) - \Gamma \, \omega^2 r \, \frac{dr}{d\hat{n}} \tag{2.1-37}$$

and

$$\frac{d\gamma}{dr} = - \Gamma \, \omega^2 r \tag{2.1-38}$$

respectively. If χ is defined as the angle between the normal and radial direction, i.e.

$$dr = d\hat{n} \cos \chi \tag{2.1-39}$$

equation (2.1-37) can be rewritten as

$$(P^G - P^L)_A = \gamma \, (\kappa_1 + \kappa_2) - \Gamma \, \omega^2 r \cos \chi \tag{2.1-40}$$

Consider now the conditions for chemical equilibrium given by equation (2.1-23). Since the variations in mole

numbers are not independent of each other, the method of Lagrange undetermined multipliers is used to solve equation (2.1-23) subject to the constraint given by equation (2.1-25). Equation (2.1-25) is multiplied by the constant λ_i, and then subtracted from equation (2.1-23) to give

$$\sum_{i=1}^{n} \int_{N_i^L} (\mu_i^L - \frac{1}{2}\omega^2 r^2 M_i - \lambda_i)\delta DN_i^L + \sum_{i=1}^{n} \int_{N_i^G} (\mu_i^G - \frac{1}{2}\omega^2 r^2 M_i - \lambda_i)\,\delta DN_i^G$$

$$+ \sum_{i=1}^{n} \int_{N_i^S} (\mu_i^S - \frac{1}{2}\omega^2 r^2 M_i - \lambda_i)\,\delta DN_i^S = 0 \qquad (2.1\text{-}41)$$

Equation (2.1-41) is satisfied by the condition that each integrand vanish, which yields

$$\mu_i^L - \frac{1}{2}\omega^2 r^2 M_i = \mu_i^G - \frac{1}{2}\omega^2 r^2 M_i$$

$$= \mu_i^S - \frac{1}{2}\omega^2 r^2 M_i = \lambda_i, \quad i=1,2, \ldots, n \qquad (2.1\text{-}42)$$

The equilibrium conditions for a gas-vapor bubble in a liquid-gas solution subject to a centrifugal field can be briefly summarized by the following equations:

$$\frac{dP^L}{dr} = -\rho^L \omega^2 r \; ; \quad \frac{dP^G}{dr} = -\rho^G \omega^2 r \tag{2.1-43}$$

$$(P^G - P^L)_A = \gamma(\kappa_1 + \kappa_2) - \Gamma\omega^2 r \cos\chi \tag{2.1-44}$$

$$\frac{d\gamma}{dr} = -\Gamma\omega^2 r \tag{2.1-45}$$

$$\mu_i^L - \frac{1}{2}\omega^2 r^2 M_i = \mu_i^G - \frac{1}{2}\omega^2 r^2 M_i = \mu_i^S - \frac{1}{2}\omega^2 r^2 M_i = \lambda_i ,$$

$$i=1, 2, \ldots, n \tag{2.1-46}$$

2.2 The Equilibrium Shape of the Gas-Vapor Bubble

The equilibrium shape of the gas-vapor bubble at the axis of rotation of the system will be deformed from a spherical shape by the centrifugal field. In this section, an expression for the equilibrium shape of the gas-vapor bubble will be derived from the conditions of equilibrium obtained in the previous section.

Since the bubble is symmetric about the axis of rotation, the curve produced by a plane section through the axis is used to represent the shape of the bubble. Figure 2.2-1 shows such a plane section. The radial direction, perpendicular to the axis of rotation, is indicated by the r-axis. The r and x intercepts are denoted by 'a' and 'b', respectively. The distance 'a' represents the maximum radius of the bubble. The radius of curvature at

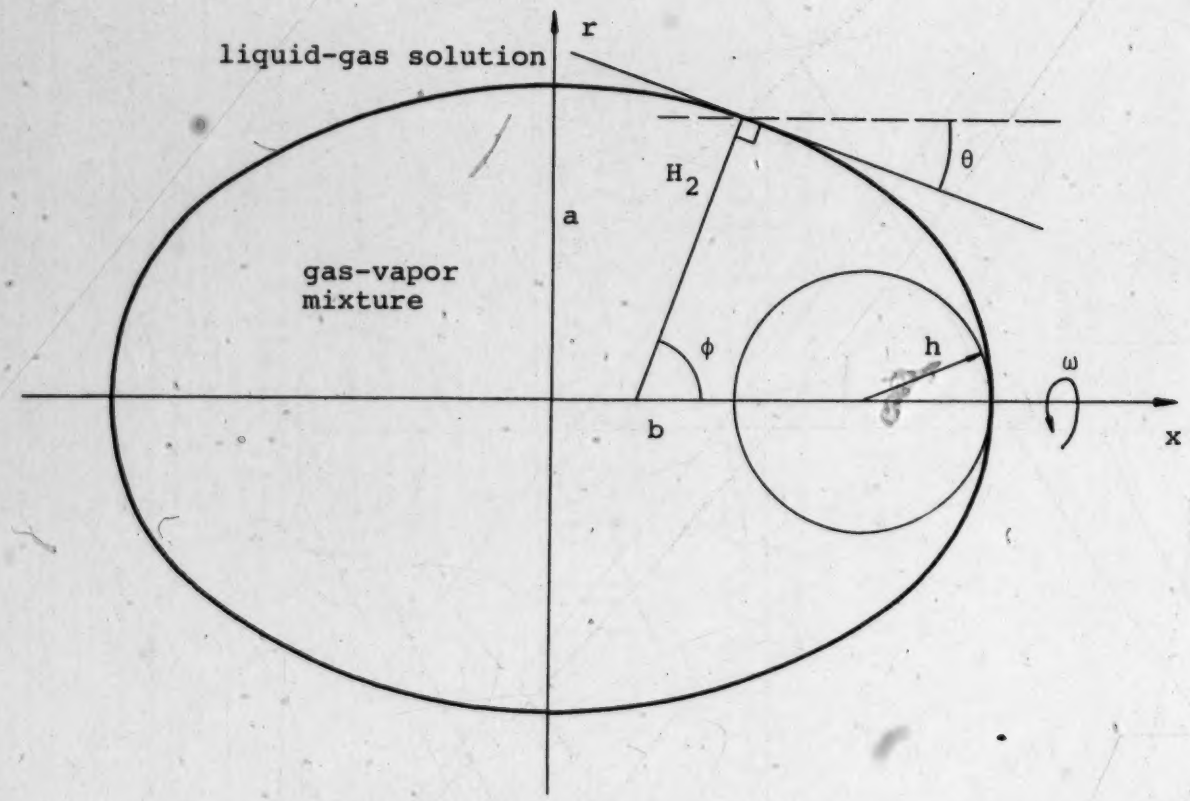

Figure 2.2-1 A Plane Section Through the Axis of Rotation of the Gas-Vapor Bubble

the center of the system, i.e. at r=0, is denoted by 'h'. The angle θ is that associated with the slope of the curve. The angle between the normal to the curve and the positive x-axis is denoted by ϕ.

Neglecting the term $\Gamma\omega^2 r\cos\chi$[7] in equation (2.1-40) results in Laplace's equation of capillarity, i.e.

$$(P^G - P^L)_A = \gamma(\kappa_1 + \kappa_2) \qquad (2.2\text{-}1)$$

relating the pressure difference across the interface to the surface tension and principal curvatures of the interface at that point. Equation (2.2-1) is further simplified by assuming the surface tension to be constant over the interface.[8] Once the pressure difference is expressed as a function of the distance r from the axis of rotation, an appropriate expression for the curvature can be substituted into equation (2.2-1) to yield a differential equation for the

---

[7]The value of the adsorption, Γ, is usually sufficiently small to justify neglecting the term $\Gamma\omega^2 r\cos\chi$ in equation (2.1-40). For example, Defay, Prigogine, and Bellemans [30] obtained a value of 0.62×10^{-10} kg-mole m^{-2} as the approximate magnitude of the relative adsorption of nitrogen at the plane surface of a saturated solution of nitrogen in water with a gaseous phase of nitrogen and water vapor.

[8]From the equilibrium conditions,

$$\frac{d\gamma}{dr} = -\Gamma\omega^2 r$$

In view of the small value of the adsorption, Γ, the radial variation of γ can be neglected.

equilibrium shape of the bubble.

Equation (2.1-34) gives the radial pressure variation in the liquid-gas solution. Integrating equation (2.1-34) from r=0 where $P^L = P_c^L$ to a point 'r' results in

$$P^L(r) = P_c^L + \frac{1}{2}\rho^L\omega^2 r^2 \qquad (2.2\text{-}2)$$

where ρ^L is constant due to the assumption of liquid incompressibility. For a gas-vapor mixture of low density, the pressure inside the bubble, P^G, can be assumed constant.[9] The pressure difference across the interface at the center of the system can be related to the radius of curvature, 'h' at that point, i.e.

$$(P^G - P_c^L)_A = \frac{2\gamma}{h} \qquad (2.2\text{-}3)$$

Using equations (2.2-2) and (2.2-3), the pressure difference across the interface at any point 'r' can be expressed as

$$(P^G - P^L)_A = \frac{2\gamma}{h} - \frac{1}{2}\rho^L\omega^2 r^2 \qquad (2.2\text{-}4)$$

---

[9] From the equilibrium conditions,

$$\frac{dP^G}{dr} = \rho^G\omega^2 r$$

For a gas-vapor mixture of low density, i.e. $\rho^G \ll 1$,

$$\frac{dP^G}{dr} \cong 0$$

implying that P^G is approximately constant.

The shape of the surface at any point is characterized by the two principal curvature, κ_1 and κ_2. For the axisymmetric surface being considered, κ_1 is the plane curvature of the meridional curve shown in Figure 2.2-1. The second curvature, κ_2, acts in a perpendicular direction to the x-r plane. The radius of curvature associated with κ_2, denoted by H_2 in Figure 2.2-1, is equal to the distance between the curve and the x-axis along a line normal to the curve in the x-r plane. From analytical geometry [31], the sum of the principal curvatures can be expressed as

$$\kappa_1 + \kappa_2 = \frac{1 + (\frac{dr}{dx})^2 - r\,(\frac{d^2r}{dx^2})}{r\,[1 + (\frac{dr}{dx})^2]^{3/2}} \qquad (2.2\text{-}5)$$

The angles θ and ϕ, positive in a counterclockwise sense, are related by the equation

$$\theta = \phi - \pi/2 \qquad (2.2\text{-}6)$$

where θ is defined by

$$\tan \theta = \frac{dr}{dx} \qquad (2.2\text{-}7)$$

Using equation (2.2-7) in (2.2-6) gives

$$\frac{dr}{dx} = -\cot \phi \qquad (2.2\text{-}8)$$

which upon differentiating yields

$$\frac{d^2r}{dx^2} = \csc^2\phi \frac{d\phi}{dx} \qquad (2.2\text{-}9)$$

Substituting expressions (2.2-8) and (2.2-9) into (2.2-5) results in

$$\kappa_1 + \kappa_2 = \frac{1 + \cot^2\phi - (r)\csc^2\phi \frac{d\phi}{dx}}{r(1 + \cot^2\phi)^{3/2}} \qquad (2.2\text{-}10)$$

which reduces to

$$\kappa_1 + \kappa_2 = \frac{1}{r}\frac{d}{dr}(r\sin\phi) \qquad (2.2\text{-}11)$$

Finally, using expressions (2.2-4) and (2.2-11) in (2.2-1) gives a differential equation for the shape of the gas-vapor bubble in terms of the parameters 'r' and ϕ, i.e.

$$\frac{1}{r}\frac{d}{dr}(r\sin\phi) = \frac{2}{h} - \frac{\rho L \omega^2 r^2}{2\gamma} \qquad (2.2\text{-}12)$$

Expression (2.2-12) can be integrated to give

$$\sin\phi = \frac{r}{h} - \frac{\rho L \omega^2 r^3}{8\gamma} \qquad (2.2\text{-}13)$$

where the constant of integration is zero since r=0 at ϕ=0. A relationship between the maximum radius of the bubble, 'a', and the radius of curvature at the center, 'h' is obtained by evaluating equation (2.2-13) at $\phi = \frac{\pi}{2}$ where r=a, i.e.

$$\frac{a}{h} = 1 + \frac{\rho L \omega^2 a^3}{8\gamma} \qquad (2.2\text{-}14)$$

Let the shape parameter 'e' be defined as

$$e \equiv \frac{\rho L \omega^2 a^3}{8\gamma} \qquad (2.2\text{-}15)$$

Then, from equation (2.2-14)

$$a = (1 + e)\, h \qquad (2.2\text{-}16)$$

and equation (2.2-13) can be expressed as

$$\sin\phi = (1 + e)R - eR^3 \qquad (2.2\text{-}17)$$

where R is the dimensionless co-ordinate given by

$$R \equiv \frac{r}{a} \qquad (2.2\text{-}18)$$

Equation (2.2-17) expresses the shape of the bubble in terms of R and ϕ, using the shape parameter 'e'.

The shape of the bubble is more conveniently expressed as an explicit function for the dimensionless co-ordinate X in terms of R, where

$$X \equiv \frac{X}{a} \qquad (2.2\text{-}19)$$

From equation (2.2-18)

$$\frac{dX}{dR} = -\tan\phi \qquad (2.2\text{-}20)$$

If $\tan\phi$ is expressed in terms of $\sin\phi$, equation (2.2-20) becomes

$$\frac{dX}{dR} = \frac{-\sin\phi}{(1 - \sin^2\phi)^{1/2}} \qquad (2.2\text{-}21)$$

Using expression (2.2-17) for $\sin\phi$ in (2.2-1) results in

$$\frac{dX}{dR} = \frac{-R[(1+e) - eR^2]}{\{1 - R^2[(1+e) - eR^2]^2\}^{1/2}} \qquad (2.2\text{-}22)$$

The solution to the differential equation represented by expression (2.2-22) can be obtained in more than one form. The expression for dX can be integrated directly in terms of elliptic integrals of the first and second kind to give a general expression for X. The result is presented in Appendix A.

However, an alternate formulation utilized by Lord Rayleigh [32] in his treatment of a rotating fluid mass subject to capillary tension expresses the solution as a series expansion in terms of the shape parameter, 'e'. Introducing the transformation

$$Z = 1 - R^2 \qquad (2.2\text{-}23)$$

into equation (2.2-22) results in

$$\frac{dX}{dZ} = \frac{1 + eZ}{2[1 - (1 - Z)(1 + eZ)^2]^{1/2}} \qquad (2.2\text{-}24)$$

The solution to equation (2.2-24) can be expressed as a series expansion in terms of powers of 'e'. For the case of a small bubble, where $e \ll 1$, only the leading terms need be retained.

An estimate of the order of magnitude of 'e' for a small negative pressure in the solution at the center of the system can be obtained using a spherical approximation for

the bubble shape. For a given system, the value of 'e' is dependent upon the maximum radius, 'a', which can be estimated using the expression for the critical radius of a spherical vapor bubble in a pure liquid [33], i.e.

$$R_c = \frac{2\gamma}{P_v - P^L} \qquad (2.2\text{-}25)$$

where P_v is the vapor pressure of the liquid. For water at 20°C, the surface tension is 0.0728 N/m and the vapor pressure is 2.34 kPa [34]. If the liquid pressure outside the bubble is -100 kPa, using equation (2.2-25), the order of magitude of 'a' is 1 μm. For an angular velocity of 1000 rad/sec,[10] the order of magnitude of the shape parameter is 10^{-9}. For larger negative pressures, the value of 'e' would be even smaller. Thus, for negative pressures in the liquid-gas solution outside the bubble, the equilibrium size of the gas-vapor bubble is sufficiently small to satisfy the condition that

$$e \ll 1 \qquad (2.2\text{-}26)$$

For such a condition, it is mathematically convenient to express the function $\frac{dX}{dZ}$ as a power series expansion in terms of 'e'. Equation (2.2-24) can be rewritten as

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[10] The value of ω strictly depends on the values of P_o and P_c^L for a given system, i.e.

$$\omega = \left[\frac{2(P_o - P_c^L)}{\rho^L \ell^2} \right]^{1/2}$$

$$\frac{dX}{dZ} = \frac{1 + eZ}{2Z^{1/2}\,[1 - 2(1-Z)e - Z(1-Z)e^2]^{1/2}} \qquad (2.2\text{-}27)$$

Using a binomial series [35] for the term

$$J \equiv [1 - 2(1-Z)e - Z(1-Z)e^2]^{-1/2} \qquad (2.2\text{-}28)$$

in equation (2.2-27) results in the following expression for J:[11]

$$J = 1 + (1-Z)e + (\tfrac{3}{2} - \tfrac{5}{2}Z + Z^2)e^2 + O(e^3) \qquad (2.2\text{-}29)$$

Using expression (2.2-29) in (2.2-27) results in

$$\frac{dX}{dZ} = \frac{1}{2Z^{1/2}}\,[1 + (1-Z)e + (\tfrac{3}{2} - \tfrac{5}{2}Z + Z^2)e^2]$$

$$+ \frac{Z^{1/2}}{2}\,[e + (1-Z)e^2] + O(e^3) \qquad (2.2\text{-}30)$$

Equation (2.2-30) can be rearranged in terms of powers of Z to give

$$\frac{dX}{dZ} = \tfrac{1}{2}(1 + e + \tfrac{3}{2}e^2)Z^{-1/2} - \tfrac{3}{4}e^2 Z^{1/2} + O(e^3) \qquad (2.2\text{-}31)$$

Transforming equation (2.2-31) back into an expression in terms of R using equation (2.2-23) gives

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[11] Expression (2.2-29) is only strictly valid for the condition $-1 < -2(1-Z) - Z(1-Z)e^2 \leq 1$. Since $0 \leq Z \leq 1$, this condition is satisfied when $e \ll 1$.

$$\frac{dX}{dR} = -\left(1 + e + \frac{3}{2}e^2\right) R(1-R^2)^{-1/2}$$

$$+ \frac{3}{2}e^2 R\,(1 - R^2)^{1/2} + O(e^3) \qquad (2.2\text{-}32)$$

Integrating equation (2.2-32) results in

$$X = \left(1 + e + \frac{3}{2}e^2\right)(1-R^2)^{1/2} - \frac{e^2}{2}(1-R^2)^{3/2} + O(e^3) \qquad (2.2\text{-}33)$$

where the constant of integration is zero since X=0 at R=1. If only terms of order 'e' are retained in equation (2.2-33), the curve produced by a plane section through the axis of the bubble can be approximated by the ellipse given by

$$\frac{X^2}{(1 + e)^2} + R^2 = 1 \qquad (2.2\text{-}34)$$

For small bubbles, where $e \ll 1$, the bubble shape is essentially that of the spheroid generated by rotating the curve given by equation (2.2-34) about the x-axis, the axis of rotation.

Briefly summarizing, this section considered the equilibrium shape of a gas-vapor bubble in a liquid-gas solution at the center of a centrifugal field. For negative pressures in the solution, the small size of the bubble led to the condition that $e \ll 1$, and the curve produced by a plane section through the axis of rotation of the bubble can be approximated by the ellipse given by equation (2.2-34).

The elongation of the bubble along the axis of rotation agrees with intuition. Due to the centrifugal field, the heavier liquid is displaced further away from the axis of rotation, causing the lighter, gaseous phase to move closer to the center of the system. Thus, the bubble is radially flattened.

In this chapter, the equilibrium state was determined from the extremum condition on the total energy of the system. The next chapter investigates the stability of this equilibrium state by considering the exact nature of the extremum condition.

CHAPTER 3

THE NATURE OF THE EQUILIBRIUM STATE

The equilibrium state is characterized by a stationary value of the total energy of the system. The stability of the equilibrium state depends upon the nature of this extremum. Minimum and maximum values of the total energy represent stable and unstable equilibrium states, respectively [35]. In order to determine the nature of the extremum, the total energy of the system must be examined for those states close to equilibrium.

Consider the difference in the total energy of the system, ΔF, between the equilibrium state, and a new state close to but not at equilibrium. The subscripts α and β will be used to denote the equilibrium and non-equilibrium states, respectively. The gas-vapor bubble in each state is characterized by a specific size and shape, as shown in Figure 3-1. From equation (2.2-34), the size and shape of the equilibrium bubble are dependent on the shape parameter, 'e', and the maximum radius, 'a'. But from equation (2.2-15) 'e' for a given system is a function of 'a'. Thus, 'a' is the obvious choice for the bubble parameter to which the state of the system is referenced. The variation of the maximum radius from the equilibrium value will indicate a displacement of the state from the equilibrium position. Let ε denote

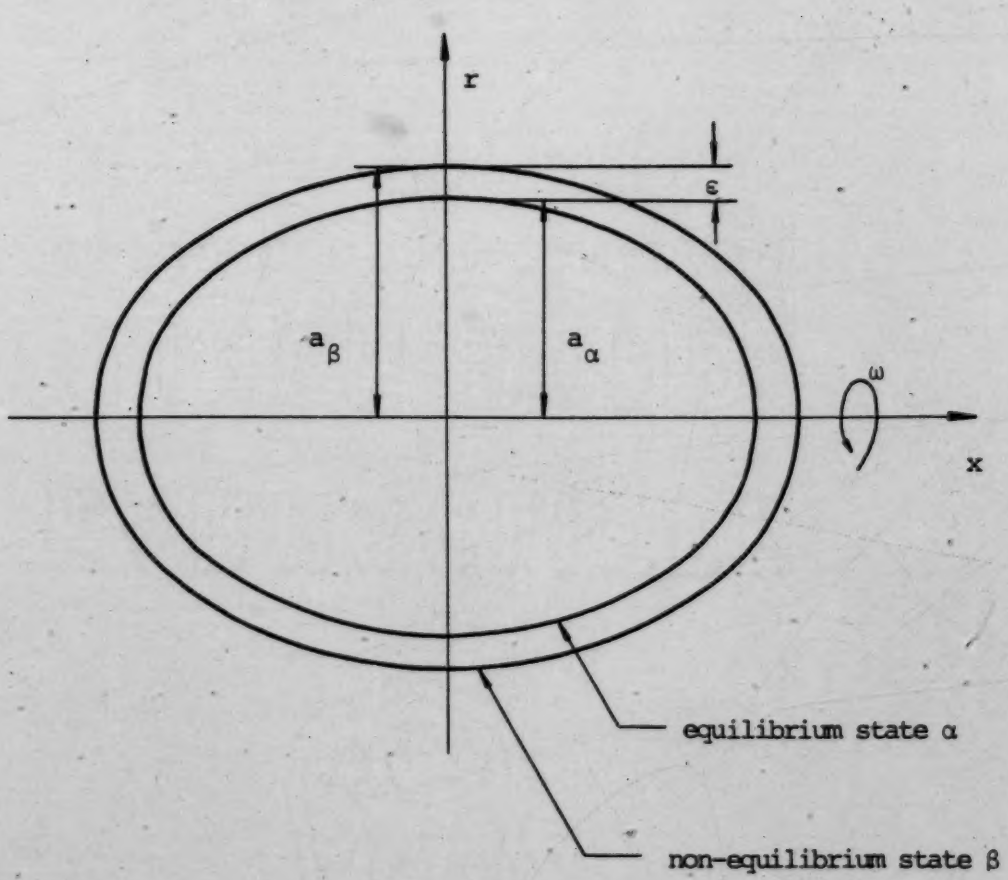

Figure 3-1 A Comparison of the Plane Sections of the Gas-Vapor Bubble in the Equilibrium and Non-Equilibrium States

the difference in the maximum radius of the bubble between the equilibrium and non-equilibrium states, i.e.

$$\varepsilon \equiv a_\beta - a_\alpha \tag{3-1}$$

where ε can be positive or negative. Using equation (3-1) in expression (2.2-15) for 'e' allows the value of the shape parameter in both states to be related, i.e.

$$e_\beta = e_\alpha \left(1 + \frac{\varepsilon}{a_\alpha}\right)^3 \tag{3-2}$$

In chapter 2 an expression was developed for the total energy of the equilibrium system, i.e.

$$F_\alpha = \int_{V_\alpha^L} - P_\alpha^L \, DV^L + \sum_{i=1}^{n} \int_{N_{i_\alpha}^L} \left(\mu_{i_\alpha}^L - \frac{1}{2}\omega^2 r^2 M_i\right) DN_i^L$$

$$+ \int_{V_\alpha^G} - P_\alpha^G \, DV^G + \sum_{i=1}^{n} \int_{N_{i_\alpha}^G} \left(\mu_{i_\alpha}^G - \frac{1}{2}\omega^2 r^2 M_i\right) DN_i^G$$

$$+ \int_{A_\alpha} \gamma_\alpha \, DA + \sum_{i=1}^{n} \int_{N_{i_\alpha}^S} \left(\mu_{i_\alpha}^S - \frac{1}{2}\omega^2 r^2 M_i\right) DN_i^S \tag{3-3}$$

For the new state[1] slightly displaced from equilibrium the total energy of the system can likewise be expressed as

$$F_\beta = \int_{V_\beta^L} - P_\beta^L \, DV^L + \sum_{i=1}^{n} \int_{N_{i_\beta}^L} (\mu_{i_\beta}^L - \tfrac{1}{2} \omega^2 r^2 M_i) \, DN_i^L$$

$$+ \int_{V_\beta^G} - P_\beta^G \, DV^G + \sum_{i=1}^{n} \int_{N_{i_\beta}^G} (\mu_{i_\beta}^G - \tfrac{1}{2} \omega^2 r^2 M_i) \, DN_i^G$$

$$+ \int_{A_\beta} \gamma_\beta \, DA + \sum_{i=1}^{n} \int_{N_{i_\beta}^S} (\mu_{i_\beta}^S - \tfrac{1}{2} \omega^2 r^2 M_i) \, DN_i^S \qquad (3\text{-}4)$$

Subtracting equation (3-3) from (3-4) gives an expression for the difference in the total energy of the system between the new and equilibrium states, i.e.

---

[1] Although the system in the displaced state is not in equilibrium as a whole, the individual phases can be assumed to exist in a state of "local equilibrium" for which the equilibrium function for the Helmholtz potential, F, is valid [37].

$$\Delta F = \int_{V_\beta^L} - P_\beta^L \, DV^L - \int_{V_\alpha^L} - P_\alpha^L \, DV^L + \int_{V_\beta^G} - P_\beta^G \, DV^G$$

$$- \int_{V_\alpha^G} - P_\alpha^G \, DV^G + \int_{A_\beta} \gamma_\beta \, DA - \int_{A_\alpha} \gamma_\alpha \, DA$$

$$+ \sum_{i=1}^{n} \int_{N_{i_\beta}^L} (\mu_{i_\beta}^L - \tfrac{1}{2} \omega^2 r^2 M_i) DN_i^L - \sum_{i=1}^{n} \int_{N_{i_\alpha}^L} (\mu_{i_\alpha}^L - \tfrac{1}{2} \omega^2 r^2 M_i) DN_i^L$$

$$+ \sum_{i=1}^{n} \int_{N_{i_\beta}^G} (\mu_{i_\beta}^G - \tfrac{1}{2} \omega^2 r^2 M_i) DN_i^G - \sum_{i=1}^{n} \int_{N_{i_\alpha}^G} (\mu_{i_\alpha}^G - \tfrac{1}{2} \omega^2 r^2 M_i) DN_i^G$$

$$+ \sum_{i=1}^{n} \int_{N_{i_\beta}^S} (\mu_{i_\beta}^S - \tfrac{1}{2} \omega^2 r^2 M_i) DN_i^S - \sum_{i=1}^{n} \int_{N_{i_\alpha}^S} (\mu_{i_\alpha}^S - \tfrac{1}{2} \omega^2 r^2 M_i) DN_i^S \qquad (3\text{-}5)$$

Consider first the pressure-volume terms in equation (3-5), i.e.

$$\int_{V_\beta^L} - P_\beta^L \, DV^L - \int_{V_\alpha^L} - P_\alpha^L \, DV^L + \int_{V_\beta^G} - P_\beta^G \, DV^G - \int_{V_\alpha^G} - P_\alpha^G \, DV^G \tag{3-6}$$

Introducing the change in volume ΔV, defined by

$$\Delta V \equiv V_\beta^G - V_\alpha^G \equiv V_\alpha^L - V_\beta^L \tag{3-7}$$

into expression (3-6) results in

$$\int_{V_\beta^L} - P_\beta^L \, DV^L - \int_{V_\beta^L} - P_\alpha^L \, DV^L - \int_{\Delta V} - P_\alpha^L \, DV^L$$

$$+ \int_{V_\alpha^G} - P_\beta^G \, DV^G + \int_{\Delta V} - P_\beta^G \, DV^G - \int_{V_\alpha^G} - P_\alpha^G \, DV^G \tag{3-8}$$

Since the bubble is very small compared to the surrounding liquid-gas solution, the pressure distribution in the liquid-gas solution in both states can be assumed equal, i.e.

$$P_\beta^L = P_\alpha^L \tag{3-9}$$

Condition (3-9) reduces expression (3-8) to

$$\int_{V_\alpha^G} - (P_\beta^G - P_\alpha^G)\, DV^G + \int_{\Delta V} - (P_\beta^G - P_\alpha^L)\, DV \qquad (3\text{-}10)$$

Now consider the chemical and field potential terms in equation (3-5), expressed by

$$\sum_{i=1}^{n} \int_{N_{i_\beta}^L} (\mu_{i_\beta}^L - \tfrac{1}{2}\omega^2 r^2 M_i) DN_i^L - \sum_{i=1}^{n} \int_{N_{i_\alpha}^L} (\mu_{i_\alpha}^L - \tfrac{1}{2}\omega^2 r^2 M_i)\, DN_i^L$$

$$+ \sum_{i=1}^{n} \int_{N_{i_\beta}^G} (\mu_{i_\beta}^G - \tfrac{1}{2}\omega^2 r^2 M_i) DN_i^G - \sum_{i=1}^{n} \int_{N_{i_\alpha}^G} (\mu_{i_\alpha}^G - \tfrac{1}{2}\omega^2 r^2 M_i)\, DN_i^G$$

$$+ \sum_{i=1}^{n} \int_{N_{i_\beta}^S} (\mu_{i_\beta}^S - \tfrac{1}{2}\omega^2 r^2 M_i) DN_i^S - \sum_{i=1}^{n} \int_{N_{i_\alpha}^S} (\mu_{i_\alpha}^S - \tfrac{1}{2}\omega^2 r^2 M_i)\, DN_i^S \qquad (3\text{-}11)$$

Since the number of molecules associated with the bubble interface is much less than the number of molecules in the gas-vapor mixture and the liquid-gas solution, the last two

terms can be neglected in expression (3-11) as small compared to the other terms. From the equilibrium conditions,

$$\mu_{i_\alpha}^{L} - \frac{1}{2}\omega^2 r^2 M_i = \mu_{i_\alpha}^{G} - \frac{1}{2}\omega^2 r^2 M_i = \lambda_i, \quad i=1,2,\ldots,n \tag{3-12}$$

where λ_i is a constant. Using equation (3-12) expression (3-11) can be written in the form

$$\sum_{i=1}^{n} \int_{N_{i_\beta}^{L}} (\mu_{i_\beta}^{L} - \frac{1}{2}\omega^2 r^2 M_i - \lambda_i)\, DN_i^{L}$$

$$+ \sum_{i=1}^{n} \int_{N_{i_\beta}^{G}} (\mu_{i_\beta}^{G} - \frac{1}{2}\omega^2 r^2 M_i - \lambda_i)\, DN_i^{G} \tag{3-13}$$

Since the temperature and pressure distribution in the liquid-gas solution in both states are equal, it follows that

$$\mu_{i_\beta}^{L} = \mu_{i_\alpha}^{L}, \quad i=1,2,\ldots,n \tag{3-14}$$

From equations (3-12) and (3-14) it is evident that the first term in expression (3-13) is equal to zero. Thus, the contribution of the chemical and field potential terms in the expression for ΔF reduces to

$$\sum_{i=1}^{n} \int_{N_{i_\beta}^G} (\mu_{i_\beta}^G - \frac{1}{2}\omega^2 r^2 M_i - \lambda_i)\, DN_i^G \qquad (3\text{-}15)$$

Finally, the surface terms in equation (3-5) consist of

$$\int_{A_\beta} \gamma_\beta\, DA - \int_{A_\alpha} \gamma_\alpha\, DA \qquad (3\text{-}16)$$

Since the surface tension is assumed constant, expression (3-16) reduces to

$$\gamma\, \Delta A \qquad (3\text{-}17)$$

where

$$\Delta A \equiv A_\beta - A_\alpha \qquad (3\text{-}18)$$

Substituting the reduced expressions for (3-6), (3-11), and (3-16) back into equation (3-5) for ΔF results in

$$\Delta F = \int_{V_\alpha^G} -(P_\beta^G - P_\alpha^G)\, DV^G + \int_{\Delta V} -(P_\beta^G - P_\alpha^L)\, DV + \sum_{i=1}^{n} \int_{N_{i_\beta}^G} (\mu_{i_\beta}^G - \frac{1}{2}\omega^2 r^2 M_i - \lambda_i)\, DN_i^G + \gamma \Delta A \qquad (3\text{-}19)$$

The pressure and the chemical potentials in the gas-vapor mixture in the equilibrium state are functions of the maximum radius, 'a', and the mole numbers, $\underset{\sim}{N}^G$, inside the bubble. The new state is considered sufficiently close to the equilibrium state to enable the pressure and chemical potentials in the gas-vapor mixture in the new state to be expressed by Taylor series expansions around the equilibrium values,[2] i.e.

$$P^G(a_\beta, \underset{\sim}{N}_\beta^G) = P^G(a_\alpha, \underset{\sim}{N}_\alpha^G) + \left.\frac{\partial P^G}{\partial a}\right|_{a_\alpha, \underset{\sim}{N}_\alpha^G} (\varepsilon) + \sum_{i=1}^{n} \left.\frac{\partial P^G}{\partial N_i^G}\right|_{a_\alpha, \underset{\sim}{N}_\alpha^G} (N_{i_\beta}^G - N_{i_\alpha}^G)$$

$$+ \text{ higher order terms} \qquad (3\text{-}20)$$

$$\mu_i^G(a_\beta, \underset{\sim}{N}_\beta^G) = \mu_i^G(a_\alpha, \underset{\sim}{N}_\alpha^G) + \left.\frac{\partial \mu_i^G}{\partial a}\right|_{a_\alpha, \underset{\sim}{N}_\alpha^G} (\varepsilon) + \sum_{j=1}^{n} \left.\frac{\partial \mu_i^G}{\partial N_j^G}\right|_{a_\alpha, \underset{\sim}{N}_\alpha^G} (N_{j_\beta}^G - N_{j_\alpha}^G)$$

$$+ \text{ higher order terms}, \quad i=1,2,\ldots,n \qquad (3\text{-}21)$$

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[2] The notation

$$\left.\frac{\partial P^G}{\partial a}\right|_{a_\alpha, \underset{\sim}{N}_\alpha^G}$$

indicates that the partial derivative of the pressure $P^G(a, \underset{\sim}{N}^G)$ with respect to 'a' is evaluated for the equilibrium values a_α and $\underset{\sim}{N}_\alpha^G$.

From the equilibrium conditions, the leading term in equation (3-21) can be expressed as

$$\mu_i^G(a_\alpha, \underset{\sim}{N}_\alpha^G) = \lambda_i + \frac{1}{2}\omega^2 r^2 M_i, \quad i=1,2,\ldots,n \tag{3-22}$$

If the higher order terms are neglected in equations (3-20) and (3-21), and the resultant expressions substituted into equation (3-19), the expression for ΔF becomes

$$\Delta F = \int_{\Delta V} -(P_\alpha^G - P_\alpha^L)\, DV + \gamma \Delta A$$

$$+ \int_{V_\alpha^G} -\left[\left.\frac{\partial P^G}{\partial a}\right|_{(\varepsilon)}_{a_\alpha, \underset{\sim}{N}_\alpha^G} + \sum_{i=1}^{n} \left.\frac{\partial P^G}{\partial N_i^G}\right|_{a_\alpha, \underset{\sim}{N}_\alpha^G} (N_{i_\beta}^G - N_{i_\alpha}^G)\right] DV^G$$

$$+ \int_{\Delta V} -\left[\left.\frac{\partial P^G}{\partial a}\right|_{(\varepsilon)}_{a_\alpha, \underset{\sim}{N}_\alpha^G} + \sum_{i=1}^{n} \left.\frac{\partial P^G}{\partial N_i^G}\right|_{a_\alpha, \underset{\sim}{N}_\alpha^G} (N_{i_\beta}^G - N_{i_\alpha}^G)\right] DV$$

$$+ \sum_{i=1}^{n} \int_{N_{i_\beta}^G} \left[\left.\frac{\partial \mu_i^G}{\partial a}\right|_{(\varepsilon)}_{a_\alpha, \underset{\sim}{N}_\alpha^G} + \sum_{j=1}^{n} \left.\frac{\partial \mu_i^G}{\partial N_j^G}\right|_{a_\alpha, \underset{\sim}{N}_\alpha^G} (N_{j_\beta}^G - N_{j_\alpha}^G)\right] DN_i^G \tag{3-23}$$

Since the quantities ε and $(\underset{\sim}{N}^G_\beta - \underset{\sim}{N}^G_\alpha)$ can be made arbitrarily small, only the first two terms will be retained as significant in equation (3-23). Then the expression for ΔF reduces to

$$\Delta F = \int_{\Delta V} - (P^G_\alpha - P^L_\alpha)\, DV + \gamma \Delta A \qquad (3\text{-}24)$$

Using expression (2.2-4) for the equilibrium pressure difference across the interface in equation (3-24) results in

$$\Delta F = \int_{\Delta V} - \left(\frac{2\gamma}{h_\alpha} - \frac{1}{2}\,\rho^L \omega^2 r^2\right) DV + \gamma \Delta A \qquad (3\text{-}25)$$

Equation (3-25) can be separated into three terms, i.e.

$$\Delta F = -J_1 + J_2 + J_3 \qquad (3\text{-}26)$$

where

$$J_1 \equiv \int_{\Delta V} \frac{2\gamma}{h_\alpha}\, DV \qquad (3\text{-}27)$$

$$J_2 \equiv \int_{\Delta V} \frac{1}{2}\,\rho^L \omega^2 r^2\, DV \qquad (3\text{-}28)$$

$$J_3 \equiv \gamma \Delta A \qquad (3\text{-}29)$$

The evaluation of J_1, J_2, and J_3 requires the use of analytical expressions for the area, volume, and a term similar to the moment of inertia of the bubble in both states. The moment of inertia, I, of an axi-symmetric body about the cylindrical axis is defined by

$$I \equiv \int_V \rho r^2 \, DV \tag{3-30}$$

The particular moment of inertia used to evaluate expression (3-28) for J_2 is that of a spheroid of liquid identical in size and shape to the gas-vapor bubble, and of constant density ρ^L. In the previous chapter it was shown that for a small bubble at negative pressures the condition $e \ll 1$ enabled the equilibrium bubble shape to be approximated by the spheroid represented by

$$\frac{x^2}{(1+e)^2 a^2} + \frac{r^2}{a^2} = 1 \tag{3-31}$$

where terms of power e^2 and higher have been neglected.[3] For this approximation, the area, volume, and moment of inertia required above are given by the following expressions:[4]

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[3]Since the original expression for the shape of the bubble has neglected terms of power e^2 and higher, these terms will not be retained in the following development.

[4]The derivations of the expressions for the area, volume, and moment of inertia are presented in Appendix B.

$$A = 4\pi a^2 \left(1 + \frac{2}{3} e\right) \tag{3-32}$$

$$V = \frac{4\pi a^3}{3} (1 + e) \tag{3-33}$$

$$I = \frac{8\pi\rho^L (1 + e) a^5}{15} \tag{3-34}$$

The expressions above are in a strict sense only valid for the equilibrium state. However, the new state will be considered sufficiently close to equilibrium to enable the equilibrium expressions for the shape, area, volume, and moment of inertia to be used in the displaced state.

Now consider the term J_1. Since both γ and h_α are constant for a given system, the integral in equation (3-27) reduces to

$$J_1 = \frac{2\gamma}{h_\alpha} (V_\beta - V_\alpha) \tag{3-35}$$

Using expression (3-33), the difference in volume can be expressed as

$$V_\beta - V_\alpha = \frac{4\pi}{3} [a_\beta^3 (1+e_\beta) - a_\alpha^3 (1+e_\alpha)] \tag{3-36}$$

Substituting expressions (3-1) and (3-2) for a_β and e_β in equation (3-36), and collecting terms results in

$$V_\beta - V_\alpha = 4\pi a_\alpha^2 (1+2e_\alpha)\varepsilon + 4\pi a (1+5e_\alpha) \varepsilon^2 + \frac{4\pi}{3} (1 + 20e_\alpha) \varepsilon^3 + O(\varepsilon^4) \tag{3-37}$$

Equation (2.2-16) expressed the equilibrium radius of curvature at the center in terms of the maximum radius and shape parameter. Substituting equations (2.2-16) and (3-37) back into (3-35), and neglecting terms of power e^2, yields an expression for J_1 in terms of the equilibrium parameters a_α and e_α, and the radial displacement ε, i.e.

$$J_1 = 8\pi\gamma a_\alpha (1 + 3e_\alpha)\varepsilon + 8\pi\gamma (1 + 6e_\alpha)\varepsilon^2 + \frac{8\pi\gamma}{3} (1 + 21e_\alpha) \frac{\varepsilon^3}{a_\alpha} + O(\varepsilon^4) \qquad (3\text{-}38)$$

Next, consider the term J_2. Using expression (3-30) in equation (3-28) gives

$$J_2 = \frac{1}{2} \omega^2 (I_\beta - I_\alpha) \qquad (3\text{-}39)$$

where the density of the spheroid considered is that of the liquid, ρ^L. Using expression (3-34) for the moment of inertia terms in (3-39) results in

$$J_2 = \frac{4\pi\rho^L\omega^2}{15} [(1 + e_\beta)a_\beta^5 - (1 + e_\alpha)a_\alpha^5] \qquad (3\text{-}40)$$

Again substituting expressions (3-1) and (3-2) for a_β and e_β in equation (3-40), and collecting terms gives

$$J_2 = \frac{4\pi\rho L\omega^2 a_\alpha^3}{15} \left[(5 + 8e_\alpha)\, a_\alpha\, \varepsilon \right.$$

$$\left. + \; 2(5 + 14e_\alpha)\varepsilon^2 + 2(5 + 28e_\alpha)\, \frac{\varepsilon^3}{a_\alpha} \right] + O(\varepsilon^4) \qquad (3\text{-}41)$$

Using the substitution

$$\rho L\omega^2 a_\alpha^3 = 8\gamma e_\alpha \qquad (3\text{-}42)$$

equation (3-41) becomes

$$J_2 = \frac{32\pi\gamma e_\alpha}{15} \left[(5 + 8e_\alpha)\, a_\alpha\, \varepsilon + 2(5 + 14e_\alpha)\varepsilon^2 \right.$$

$$\left. + \; 2(5 + 28e_\alpha)\, \frac{\varepsilon^3}{a_\alpha} \right] + O(\varepsilon^4) \qquad (3\text{-}43)$$

Neglecting powers of e^2 reduces expression (3-43) for J_2 to

$$J_2 = \frac{32\pi\gamma e_\alpha}{15} \left(a_\alpha \varepsilon + 2\varepsilon^2 + 2\, \frac{\varepsilon^3}{a_\alpha} \right) + O(\varepsilon^4) \qquad (3\text{-}44)$$

Finally, consider the term J_3. Using expression (3-32) for the area in (3-29) results in

$$J_3 = 4\pi\gamma \left[a_\beta^2 \left(1 + \frac{2}{3}\, e_\beta\right) - a_\alpha^2 \left(1 + \frac{2}{3}\, e_\alpha\right) \right] \qquad (3\text{-}45)$$

Substituting expressions (3-1) and (3-2) for a_β and e_β in the above equation yields the following expression for J_3:

$$J_3 = 8\pi\gamma a_\alpha \left(1 + \frac{5}{3} e_\alpha\right) \varepsilon + 4\pi\gamma \left(1 + \frac{20}{3} e_\alpha\right)\varepsilon^2$$

$$+ \frac{80}{3} \pi\gamma e_\alpha \frac{\varepsilon^3}{a_\alpha} + O(\varepsilon^4) \qquad (3\text{-}46)$$

Returning to expression (3-26), and substituting for J_1, J_2, and J_3 from equations (3-38), (3-44), and (3-46), respectively, results in an expression for ΔF close to equilibrium, i.e.

$$\Delta F = 4\pi\gamma a_\alpha^2 \left[-\left(\frac{\varepsilon}{a_\alpha}\right)^2 - \frac{2}{3} \left(1 + 3e_\alpha\right) \left(\frac{\varepsilon}{a_\alpha}\right)^3 \right] + O(\varepsilon^4) \qquad (3\text{-}47)$$

where $\left(\frac{\varepsilon}{a_\alpha}\right) \ll 1$.

Expression (3-47) retains terms of $O(\varepsilon^4)$. As a means of determining how many terms must be retained in equation (3-47), the expression for ΔF when no field is present can be compared to that obtained by Ward *et al.* [38] for the case of positive pressures in the liquid-gas solution. When the angular velocity is zero, the shape parameter is zero, and equation (3-47) reduces to

$$\Delta F = 4\pi\gamma a_\alpha^2 \left[-\left(\frac{\varepsilon}{a_\alpha}\right)^2 - \frac{2}{3} \left(\frac{\varepsilon}{a_\alpha}\right)^3 \right] + O(\varepsilon^4) \qquad (3\text{-}48)$$

Ward et al. obtained the following expression[5] for the difference in the free energy of the equilibrium and non-equilibrium systems:

$$\Delta F = 4\pi\gamma \left(R^2 - \frac{1}{3} R_c^2 - \frac{2}{3} \frac{R^3}{R_c}\right) \tag{3-49}$$

where R_c and R are, respectively, the radii of the spherical gas-vapor bubble in the equilibrium and non-equilibrium states. For means of comparison, the expression

$$R = R_c + \varepsilon \tag{3-50}$$

can be substituted into equation (3-49) to give

$$\Delta F = 4\pi\gamma R_c^2 \left[- \left(\frac{\varepsilon}{R_c}\right)^2 - \frac{2}{3} \left(\frac{\varepsilon}{R_c}\right)^3 \right] \tag{3-51}$$

Comparing equations (3-48) and (3-51), and noting that for zero angular velocity, $a_\alpha = R_c$, it is evident that

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[5] Ward et al. obtained the following expression for the change in the Helmholtz potential, ΔF_o, due to the formation of a spherical gas-vapor bubble of radius R close to the equilibrium radius, R_c, in a liquid-gas solution:

$$\Delta F_o = 4\pi\gamma \left(R^2 - \frac{2}{3} \frac{R^3}{R_c}\right)$$

In order to obtain the difference in the Helmholtz potential between the equilibrium and non-equilibrium states, the reversible work, W_R, for the formation of the equilibrium bubble must be subtracted from the equation above. The reversible work is obtained from the equation above evaluated at $R = R_c$, i.e.

$$W_R = \frac{4\pi\gamma R_c^2}{3}$$

expression (3-47) for ΔF reduces to that of Ward et al. for the no field condition. Terms of $O(\varepsilon^4)$ can be neglected in equation (3-47), and the expression for ΔF reduces to

$$\Delta F = 4\pi\gamma a_\alpha^2 \left[- \left(\frac{\varepsilon}{a_\alpha}\right)^2 - \frac{2}{3} (1 + 3e_\alpha) \left(\frac{\varepsilon}{a_\alpha}\right)^3 \right] \qquad (3\text{-}52)$$

Since equation (3-52) represents the change in the free energy of the system as a function of the radial displacement ε, it can be used to determine the nature of the extremum at equilibrium, i.e. at $\varepsilon=0$. Differentiating equation (3-52) twice with respect to ε gives

$$\frac{d(\Delta F)}{d\varepsilon} = 4\pi\gamma a_\alpha \left[- 2 \frac{\varepsilon}{a_\alpha} - 2(1 + 3e_\alpha) \left(\frac{\varepsilon}{a_\alpha}\right)^2 \right] \qquad (3\text{-}53)$$

and

$$\frac{d^2(\Delta F)}{d\varepsilon} = 4\pi\gamma \left[- 2 - 4 (1 + 3e_\alpha) \left(\frac{\varepsilon}{a_\alpha}\right) \right] \qquad (3\text{-}54)$$

Setting $\frac{d(\Delta F)}{d\varepsilon}$ equal to zero yields the stationary value, $\varepsilon=0$, for which $\frac{d^2(\Delta F)}{d\varepsilon^2}$ is less than zero. Thus, the extremum for the free energy of the system at equilibrium is a maximum. Figure 3-2 shows the graph of equation (3-52) in the region close to $\varepsilon=0$ for $e = 10^{-6}$.

Since the free energy of the system is a maximum for $\varepsilon=0$, the equilibrium state of the gas-vapor bubble is unstable. The condition of instability leads to the concept of a critical size for the bubble, characterized by the

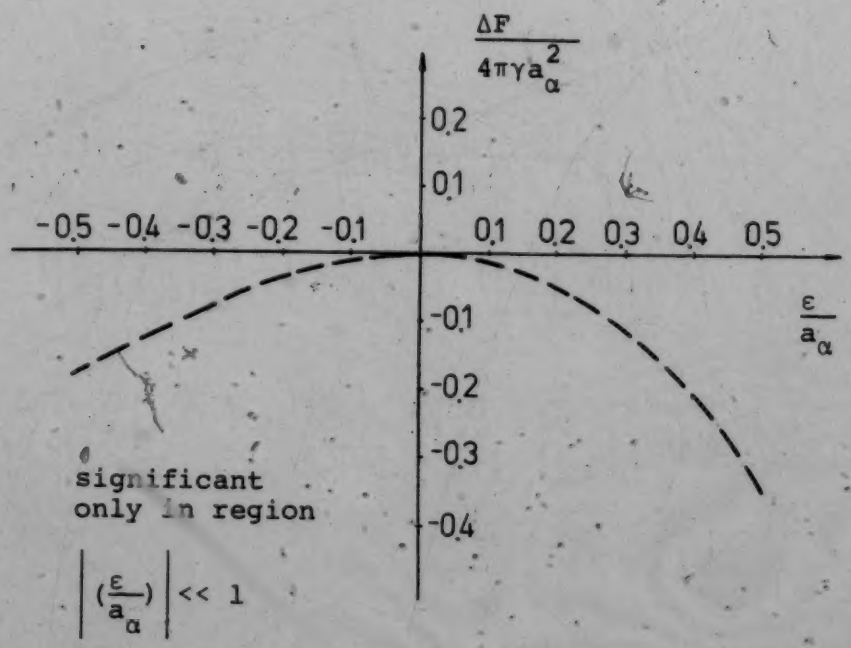

Figure 3-2 The Behavior of the Helmholtz Potential in the Neighborhood of the Equilibrium State for Which ε Equals Zero. The value of the shape parameter 'e' is 1×10^{-6}

equilibrium value of the maximum radius, a_α. If a bubble is created of less than equilibrium size, the decrease in energy accompanying bubble contraction causes the bubble to spontaneously collapse. Likewise, if a bubble is created of greater than equilibrium size, the decrease in energy accompanying bubble expansion causes the bubble to spontaneously grow. In this sense, the equilibrium size represents a critical value which must be exceeded if the bubble is to grow.

Stability considerations have shown that the free energy of the gas-vapor bubble is a maximum for the equilibrium state. The reversible work of formation, W_R, for the equilibrium gas-vapor bubble represents the increase in the free energy of the equilibrium system due to the formation of the gas-vapor bubble. An expression can be obtained for W_R by comparing the Helmholtz potential, F_α, of the equilibrium system with the Helmholtz potential of the liquid-gas solution without the bubble present. The difference in free energy between the two systems represents the work required to form the equilibrium gas-vapor bubble. If the subscript ν is used to denote the equilibrium system consisting of only the liquid-gas solution, the expression for F_ν is expressed by

$$F_\nu = \int_{V_\nu^L} P_\nu^L \, DV^L + \sum_{i=1}^{n} \int_{N_{i_\nu}^L} (\mu_{i_\nu}^L - \frac{1}{2} \omega^2 r^2 M_i) \, DN_i^L \qquad (3\text{-}55)$$

The condition of chemical equilibrium in the liquid-gas solution requires that

$$\mu_{i_\nu}^L - \frac{1}{2}\omega^2 r^2 M_i = \lambda_{i_\nu}, \quad i=1,2,\ldots,n \tag{3-56}$$

where λ_{i_ν} is a constant. Using expression (3-56) in (3-55) gives

$$F_\nu = \int_{V_\nu^L} - P_\nu^L \, DV^L + \sum_{i=1}^{n} \lambda_{i_\nu} N_{i_\nu}^L \tag{3-57}$$

Equation (2.1-42) for the condition of chemical equilibrium in the system with the bubble present can be used to reduce expression (3-3) for F_α to

$$F_\alpha = \int_{V_\alpha^L} - P_\alpha^L \, DV^L + \int_{V_\alpha^G} - P_\alpha^G \, DV^G + \int_A \gamma DA + \sum_{i=1}^{n} \lambda_i N_i^T \tag{3-58}$$

Subtracting expression (3-57) for F_ν from (3-58) for F_α gives the following expression for the reversible work of formation for the equilibrium gas-vapor bubble:

$$W_R = \int_{V_\alpha^L} - P_\alpha^L \, DV^L + \int_{V_\alpha^G} - P_\alpha^G \, DV^G - \int_{V_\nu^L} - P_\nu^L \, DV^L$$

$$+ \int_A \gamma DA + \sum_{i=1}^{n} [\, \lambda_{i_\alpha} N_{i_\alpha}^T - \lambda_{i_\nu} N_{i_\nu}^L] \qquad (3\text{-}59)$$

Noting that

$$V_\nu^L = V_\alpha^L + V_\alpha^G \qquad (3\text{-}60)$$

and

$$N_{i_\nu}^L = N_{i_\alpha}^T \qquad (3\text{-}61)$$

in equation (3-59) results in

$$W_R = \int_{V_\alpha^L} - (P_\alpha^L - P_\nu^L) \, DV^L + \int_{V_\alpha^G} - (P_\alpha^G - P_\nu^L) \, DV^G$$

$$+ \int_A \gamma DA + \sum_{i=1}^{n} \gamma(\lambda_{i_\alpha} - \lambda_{i_\nu}) \, N_{i_\alpha}^T \qquad (3\text{-}62)$$

Since the bubble is very small in comparison to the surrounding solution, the pressure distribution in the

liquid-gas solution in both systems can be assumed equal, i.e.

$$P_{\alpha}^{L} = P_{\nu}^{L} \tag{3-63}$$

The equality of the pressure distribution and temperature in the liquid-gas solution in both systems implies that

$$\mu_{i_{\alpha}}^{L} = \mu_{i_{\nu}}^{L} \quad , \; i=1,2,\ldots,n \tag{3-64}$$

Using expressions (3-12) and (3-56) in equation (3-64) results in

$$\lambda_{i_{\alpha}} = \lambda_{i_{\nu}} \quad , \; i=1,2,\ldots,n \tag{3-65}$$

Equations (3-63) and (3-65) are used to reduce expression (3-62) for W_R to

$$W_R = \int_{V_{\alpha}^{G}} - (P_{\alpha}^{G} - P_{\alpha}^{L}) \, DV^{G} + \int_{A} \gamma DA \tag{3-66}$$

Using expression (2.2-4) for the pressure difference across the equilibrium interface, and noting that γ is constant in expression (3-66) results in

$$W_R = \int_{V_{\alpha}^{G}} - \left(\frac{2\gamma}{h_{\alpha}} - \frac{1}{2} \rho^{L} \omega^{2} r^{2} \right) DV + \gamma A \tag{3-67}$$

or upon rearranging,

$$W_R = -\frac{2\gamma V}{h_\alpha} + \frac{1}{2}\omega^2 \int_V \rho_L r^2 \, DV + \gamma A \qquad (3\text{-}68)$$

where V and A refer to the equilibrium bubble. Substituting expression (3-33) for V, and expression (2.2-16) for h_α in the first term of equation (3-68) gives

$$-\frac{2\gamma V}{h_\alpha} = -\frac{8\pi\gamma a_\alpha^2}{3}(1 + 2e_\alpha) \qquad (3\text{-}69)$$

where powers of e_α^2 have been neglected. If the integral in the second term of equation (3-68) is evaluated using expression (3-34) for the moment of inertia, the resultant expression is

$$\frac{1}{2}\omega^2 \int_V \rho_L r^2 \, DV = \frac{4\pi\rho_L \omega^2 a_\alpha^5 (1 + e)}{15} \qquad (3\text{-}70)$$

Using expression (3-42) in (3-70), and neglecting powers of e_α^2 results in

$$\frac{1}{2}\omega^2 \int_V \rho_L r^2 \, DV = \frac{32\pi\gamma a_\alpha^2 e_\alpha}{15} \qquad (3\text{-}71)$$

Substituting expression (3-32) for A in the last term of equation (3-68) gives

$$\gamma A = 4\pi\gamma a_\alpha^2 \left(1 + \frac{2}{3} e_\alpha\right) \qquad (3\text{-}72)$$

Finally, using expressions (3-69), (3-71), and (3-72) in (3-68) yields an expression for the reversible work of formation for the equilibrium gas-vapor bubble, i.e.

$$W_R = \frac{4\pi\gamma a_\alpha^2}{3} \left(1 - \frac{2}{5} e_\alpha\right) \qquad (3\text{-}73)$$

In summary, the stability analysis determined that the free energy of a gas-vapor bubble in a liquid-gas solution at negative pressure is a maximum for the equilibrium state. Consequently, the equilibrium state is unstable, and the equilibrium size of the bubble represents a critical value. A gas-vapor bubble must exceed the critical size in order to spontaneously grow. The reversible work required to form a gas-vapor bubble of critical size is expressed by equation (3-73).

In the next chapter, an expression is developed for the critical size of a gas-vapor bubble in a dilute, liquid-gas solution at negative pressure in terms of the properties of the solution.

CHAPTER 4

THE CRITICAL SIZE OF A GAS-VAPOR BUBBLE IN A DILUTE SOLUTION AT NEGATIVE PRESSURES

In chapter 2 an expression for the equilibrium shape of the gas-vapor bubble was obtained from the conditions of equilibrium. For the case of negative pressures in the solution at the center of the system, $e << 1$, and the bubble was approximated by the spheroid represented by equation (2.2-34). In the case of a spherical bubble when no field is present, the size is expressed in terms of the equilibrium or critical radius [39]. For a spheroidal bubble, equation (2.2-34) expresses the equilibrium size and shape as a function of the maximum radius 'a'.

Since the bubble size and shape is an equilibrium property of the system, it is appropriate to develop an expression for 'a' in terms of the properties of the liquid-gas solution. However, the value of 'a' is implicitly expressed by the cubic equation given by (2.2-14), which depends upon the radius of curvature at the center of the bubble, 'h'. Thus, 'h' is the basic parameter, which when evaluated in terms of the properties of the solution, enables the size and shape of the equilibrium gas-vapor bubble to be determined. As the bubble--and hence the shape parameter--becomes smaller and smaller, the deviation from sphericity becomes practically

negligible. For a perfectly spherical bubble, the radius and radius of curvature are equal. In practice, since e << 1, evaluation of 'h' in terms of the solution properties will be sufficient to describe the equilibrium size of the bubble.

Up until now, the analysis has been of a general nature, i.e. the equilibrium and stability considered the case of a multicomponent liquid-gas solution. At this point, the development will be restricted to the specific case of a dilute solution of a single gas in a liquid solvent. The term dilute implies that the number of solute molecules is much less than the number of solvent molecules, and consequently, any interaction among the solute molecules may be ignored [40]. The concentration, C, of the solution is defined as the ratio of the number of moles of solute to the number of moles of solvent, i.e.

$$C \equiv \frac{N_2^L}{N_1^L} \tag{4-1}$$

where the subscripts 1 and 2 refer to the liquid and gas components, respectively. For a dilute solution,

$$C << 1 \tag{4-2}$$

In addition, it is assumed that the gas and vapor inside the bubble behave as an ideal gas mixture. Using appropriate

expressions for the properties of a dilute solution and an ideal gas mixture, an expression for 'h' can be developed in terms of the liquid phase properties.

The value of 'h' is obtained from Laplace's equation of capillarity, given by (2.2-1), evaluated at the center of the system where the bubble curvature is $\frac{2\gamma}{h}$. Rearranging equation (2.2-3) gives

$$h = \frac{2\gamma}{(P_c^G - P_c^L)} \qquad (4-3)$$

Integrating equation (2.1-34) from r=ℓ where $P^L = P_o$ to r=0 yields an expression for P_c^L, the pressure in the liquid at the center of the system, i.e.

$$P_c^L = P_o - \frac{1}{2}\rho^L\omega^2\ell^2 \qquad (4-4)$$

It remains to obtain an expression for P_c^G in terms of the properties of the dilute solution.

The partial pressures of the gas and vapor components inside the bubble can be expressed in terms of their respective mole fractions, X_1 and X_2, i.e.

$$P_i^G \equiv P^G X_i \quad , \quad i=1,2 \qquad (4-5)$$

where

$$X_i \equiv \frac{N_i}{N} \quad , \quad i=1,2 \qquad (4-6)$$

and

$$N = N_1 + N_2 \tag{4-7}$$

The total pressure, P^G, is the sum of the partial pressures, i.e.

$$P^G = P_1^G + P_2^G \tag{4-8}$$

The expressions for the partial pressures are obtained from the condition of chemical equilibrium across the interface, i.e.

$$\mu_i^L - \frac{1}{2}\omega^2 r^2 M_i = \mu_i^G - \frac{1}{2}\omega^2 r^2 M_i, \quad i=1,2 \tag{4-9}$$

The general expression for the chemical potential of each component in an ideal gas mixture is

$$\mu_i(P,T) = \mu_{0i}^G(P_r,T) + kT \ln\left(\frac{PX_i}{P_r}\right) \tag{4-10}$$

where 'k' is Boltzmann's constant and $\mu_{0i}^G(P_r,T)$ is the chemical potential of the pure component at some reference pressure P_r [41].

For a dilute solution of concentration C, the chemical potentials of the solvent and solute can be expressed respectively as

$$\mu_1(P,T) = \mu_{01}^L(P,T) - kTC \tag{4-11}$$

and

$$\mu_2(P,T) = \psi(P,T) + kT \ln C \tag{4-12}$$

where $\mu_{01}^{L}(P,T)$ is the chemical potential of the pure liquid component, and $\psi(P,T)$ is a function of P and T [42]. For an incompressible solvent with specific volume v^L, a reference pressure, P_r, can be introduced into expression (4-11) to give

$$\mu_1(P,T) = \mu_{01}^{L}(P_r,T) + v^L (P - P_r) - kTC \qquad (4\text{-}13)$$

Now evaluating equation (4-9) at the interface yields the condition of equality of chemical potentials across the interface, i.e.

$$\mu_i^L = \mu_i^G , \quad i=1,2 \qquad (4\text{-}14)$$

Substituting the appropriate expressions for the chemical potentials in the equation above results in expressions for the partial pressures in terms of the properties of the dilute solution.

Consider first component 1. Choosing P_v, the vapor pressure of the liquid, as the reference pressure, and using expression (4-10) and (4-13) in (4-14) gives

$$\mu_{01}^{L}(P_v,T) + v^L (P^L - P_v) - kTC$$

$$= \mu_{01}^{G}(P_v,T) + kT \ln \left(\frac{P^G X_1}{P_v}\right) \qquad (4\text{-}15)$$

Noting that $\mu_{01}^{L}(P_v,T) = \mu_{01}^{G}(P_v,T)$[1] and rearranging equation (4-15) results in an expression for the partial pressure of the vapor inside the bubble, i.e.

$$P^{G}X_1 = P_v \exp\left[\frac{v^{L}}{kT}(P^{L} - P_v) - C\right] \qquad (4\text{-}16)$$

Now consider component 2. Using expressions (4-10) and (4-12) in (4-14) gives

$$kT \ln\left(\frac{P^{G}X_2}{P_r}\right) = \psi(P^{L},T) - \mu_{02}^{G}(P_r,T) + kT \ln C \qquad (4\text{-}17)$$

The functions $\psi(P^{L},T)$ and $\mu_{02}^{G}(P_r,T)$ are unknown in terms of the properties of the dilute solution. Therefore, a reference condition will be used to eliminate the term $\psi(P^{L},T) - \mu_{02}^{G}(P_r,T)$ from expression (4-17). Since the equilibrium size and shape of the bubble pertain to negative pressures in the surrounding solution, the reference condition must remain valid when the liquid near the center of the system enters a state of tension.

Ward et al. [44] considered a reference system consisting of a liquid saturated with the gas component across a flat interface. The pure gas and liquid phases

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[1] The vapor pressure is the pressure of the vapor in equilibrium with a liquid phase for a flat interface at a given temperature [43]. Since the system is in equilibrium, it follows that the chemical potentials in each phase are equal.

were separated by a non-rigid membrane permeable only to the gas component. For such a system at equilibrium, the equality of the chemical potential of the gas component across the interface enabled the following substitution to be made in equation (4-17) with the reference pressure chosen to be P^L:

$$\psi(P^L,T) - \mu_{02}^{G}(P^L,T) = -kT \ln C_o \qquad (4\text{-}18)$$

where C_o is the saturation concentration of the gas in the liquid phase. However, such a reference condition is not appropriate to a system where the dilute solution outside the bubble is subject to negative pressures. Since the membrane in the reference system is flat, a state of tension in the solution would require the pressure in the gas phase to also be negative, which is impossible. Thus, the reference concentration used by Ward et al. in their treatment of an equilibrium gas-vapor bubble is not defined for the case of negative pressures in the solution outside the bubble.

Consider instead the reference system given in Figure 4-1, where the non-rigid membrane at $r=\ell$ is only permeable to the gas component. The liquid and gas subsystems are denoted by the superscripts LR and GR, respectively. Since the geometry, angular velocity, and reference pressure in the primary and reference systems are the same, the pressure distributions in the liquid-gas solution are identical. The condition of chemical equilibrium for the

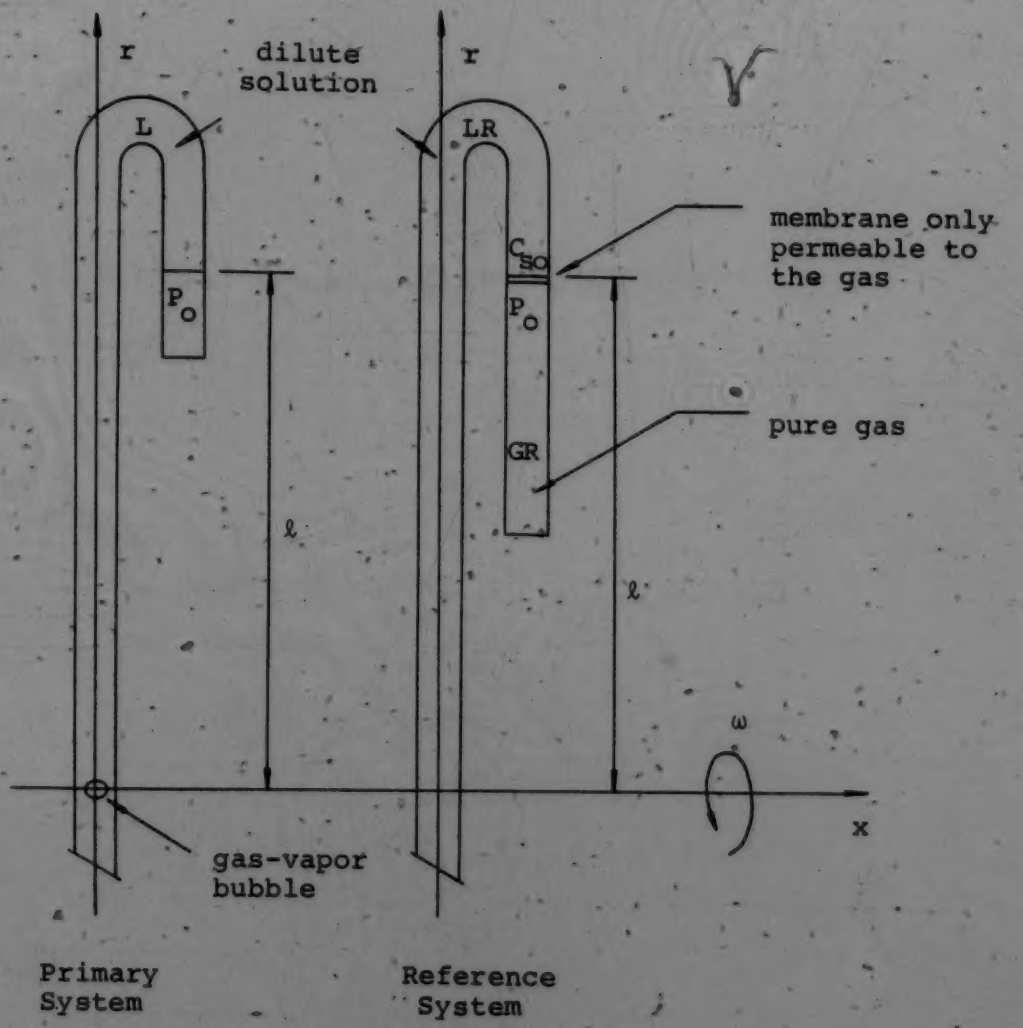

Figure 4-1 A Comparison of the Primary and Reference Systems

gas component in the reference system requires that

$$\mu_2^{LR} - \frac{1}{2}\omega^2 r^2 M_2 = \mu_2^{GR} - \frac{1}{2}\omega^2 r^2 M_2 \qquad (4\text{-}19)$$

Specifically, consider condition (4-19) for a point 'r' in the liquid solution and the point $r=\ell$ in the gas at the membrane. Using the expressions for the chemical potential of the gas component in each subsystem in equation (4-19) gives

$$\psi(P^{LR},T) + kT\ell n C_s - \frac{1}{2}\omega^2 r^2 M_2 = \mu_{02}^{G}(P_o,T) - \frac{1}{2}\omega^2 \ell^2 M_2 \qquad (4\text{-}20)$$

where P_o is the reference pressure at the membrane, and C_s is the equilibrium concentration at any point 'r' in the reference system. Rearranging equation (4-20) and noting that P^{LR} is equal to P^L, results in

$$\psi(P^L,T) - \mu_{02}^{G}(P_o,T) = kT\ell n\left(\frac{1}{C_s}\right) + \frac{1}{2}\omega^2(r^2 - \ell^2)M_2 \qquad (4\text{-}21)$$

Knowledge of the equilibrium distribution of the gas in the reference system allows the concentration C_s at 'r' to be related to the concentration C_{so} at the membrane. The expression for the equilibrium concentration, C_s, is obtained from the conditions of equilibrium in the dilute solution in the reference system, i.e.

$$\frac{dP^{LR}}{dr} = \rho^L \omega^2 r \qquad (4\text{-}22)$$

and

$$\mu_2^{LR} - \frac{1}{2}\omega^2 r^2 M_2 = \lambda_2^R \qquad (4\text{-}23)$$

where λ_2^R is a constant. Using the expression for the chemical potential of the solute in a dilute solution in equation (4-23) results in

$$\psi(P^{LR},T) + kT \ln C_s - \frac{1}{2}\omega^2 r^2 M_2 = \lambda_2^R \qquad (4\text{-}24)$$

Differentiating expression (4-24) with respect to 'r' at constant temperature yields

$$\frac{\partial \psi}{\partial P^{LR}} \frac{dP^{LR}}{dr} + \frac{kT}{C_s} \frac{dC_s}{dr} - \omega^2 r M_2 = 0 \qquad (4\text{-}25)$$

where $\frac{d\lambda_2^R}{dr} = 0$, since λ_2^R is a constant. Substituting expression (4-22) for $\frac{dP^{LR}}{dr}$ in (4-25), and rearranging gives

$$kT \frac{dC_s}{C_s} = (M_2 - \rho^L \frac{\partial \psi}{\partial P^{LR}}) \omega^2 r dr \qquad (4\text{-}26)$$

From equation (4-12),

$$\frac{\partial \psi}{\partial P^{LR}} = \frac{\partial \mu_2}{\partial P^{LR}}\Bigg|_{T,N_1,N_2} \qquad (4\text{-}27)$$

Using the relations $\mu_2 = \frac{\partial G}{\partial N_2}\Big|_{T,P,N_1}$ and

$V = \left.\frac{\partial G}{\partial P}\right|_{T,N_1,N_2}$ [45][2] reduces equation (4-27) to

$$\frac{\partial \psi}{\partial P^{LR}} = \bar{V}_2 \qquad (4\text{-}28)$$

where $\bar{V}_2$ is the partial molar volume of the gas in the dilute solution, i.e.

$$\bar{V}_2 = \left.\frac{\partial V}{\partial N_2}\right|_{T,P,N_1} \qquad (4\text{-}29)$$

Substituting expression (4-29) into (4-26) results in

$$kT \frac{dC_s}{C_s} = (M_2 - \rho^L \bar{V}_2)\, \omega^2 r\, dr \qquad (4\text{-}30)$$

Integrating equation (4-30) from $r=\ell$ where $C_s = C_{so}$, to a point 'r' in the solution gives

$$C_s = C_{so} \exp\left[\frac{\omega^2}{2kT}(\ell^2 - r^2)(\rho^L \bar{V}_2 - M_2)\right] \qquad (4\text{-}31)$$

where ρ^L and $\bar{V}_2$ are assumed to be constant. The concentration C_{so} can be evaluated using Henry's law constant, K_H [46], i.e.

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[2]The symbol G denotes the Gibbs potential, which is the Legendre transformation of the internal energy replacing the entropy by the temperature and volume by the pressure as the independent variables, i.e.

$$G = U - TS - PV$$

$$C_{so} = \frac{P_o}{K_H(T)} \qquad (4\text{-}32)$$

once P_o is specified. Before returning to the primary system, the contribution of the reference system can be briefly summarized. Equation (4-21) represents a useful substitution for the unknown quantity $\psi(P^L,T) - \mu_{02}^G(P_o,T)$ in equation (4-17) for the primary system. The reference concentration, C_s, expressed by equation (4-31), is valid for the case of negative pressures in the liquid-gas solution outside the bubble.

Returning to the primary system, let the reference pressure in equation (4-17) be equal to P_o. Then, using equation (4-21) in (4-17) results in

$$kT \ln \left(\frac{P^G X_2}{P_o}\right) = kT \ln \left(\frac{C}{C_s}\right) + \frac{1}{2}\omega^2(r^2 - \ell^2)M_2 \qquad (4\text{-}33)$$

Substituting equations (4-31) and (4-32) in (4-33), and rearranging yields an expression for the partial pressure of the gas inside the bubble, i.e.

$$P^G X_2 = C K_H \exp\left[\frac{\rho^L \omega^2 \bar{V}_2}{2kT}(r^2 - \ell^2)\right] \qquad (4\text{-}34)$$

Using equations (4-16) and (4-34) for the partial pressures in (4-8) results in an expression for the total pressure, P^G, inside the bubble in terms of the properties of the liquid-gas solution, i.e.

$$P^G = \eta_1 P_v + \eta_2 \, C \, K_H \tag{4-35}$$

where

$$\eta_1 \equiv \exp\left[\frac{v^L}{kT} (P^L - P_v) - C \right] \tag{4-36}$$

and

$$\eta_2 \equiv \exp\left[\frac{\rho^L \omega^2 \overline{V}_2}{2kT} (r^2 - \ell^2) \right] \tag{4-37}$$

Expression (4-3) for 'h' requires the value of P^G at the center of the system, P^G_c. Setting 'r' equal to zero in equation (4-35) gives

$$P^G_c = \xi_1 P_v + \xi_2 \, C \, K_H \tag{4-38}$$

where ξ_1 and ξ_2 are defined to be the values of η_1 and η_2, respectively, at r=0, i.e.

$$\xi_1 \equiv \exp\left[\frac{v^L}{kT} (P^L_c - P_v) - C \right] \tag{4-39}$$

and

$$\xi_2 \equiv \exp\left[- \frac{\rho^L \omega^2 \ell^2 \overline{V}_2}{2kT} \right] \tag{4-40}$$

Due to the low density of the gas-vapor mixture inside the bubble, the pressure P^G was previously assumed to be constant and equal to the value at the center. It should be noted that this is equivalent to approximating η_1 and η_2 by their values at the center, i.e.

$$\eta_1 \cong \xi_1 \tag{4-41}$$

$$\eta_2 \cong \xi_2 \tag{4-42}$$

where $r^2 << \ell^2$ in equations (4-36) and (4-37).[3]

Equation (4-40) relates ξ_2 to the angular velocity and the length of the system. For a given system operating at a specific speed, both ω and ℓ are constants. Since it is preferable to express ξ_2 as a function of the thermodynamic variables, equation (4-4) will be used to eliminate the term $\frac{1}{2}\rho^L\omega^2\ell^2$ from equation (4-40). The resultant equation expresses ξ_2 as a function of the pressure in the dilute solution, i.e.

$$\xi_2 = \exp\left[\frac{(P_c^L - P_o)\bar{V}_2}{kT}\right] \tag{4-43}$$

The concentration C in equation (4-38) specifically refers to that in the liquid-gas solution at the center of the system. In practice, the solution is initially placed in the tube of the centrifugal system at rest,

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[3] From equation (4-4), a negative pressure in the liquid-gas solution at the center of the system requires that

$$\frac{1}{2}\rho^L\omega^2\ell^2 > P_o$$

Due to practical limitations on the angular velocity, ω, in experimental systems, the length, ℓ, is usually several orders of magnitude greater than the equilibrium size of the bubble. Thus, for experimental systems such as that of Briggs [47],

$$r^2 << \ell^2$$

and the concentration is everywhere the same. Then the system is quickly accelerated to the angular velocity required. Since the time scale for the diffusion of a gas in a liquid is much greater than that for the attainment of mechanical equilibrium,[4] the concentration of the gas remains constant throughout the solution over the time span of the experiment. Thus, C is considered to be a given quantity in expression (4-38).

Substituting equation (4-38) back into (4-3) yields an expression for 'h' in terms of the properties of the dilute solution for a given system, i.e.

$$h = \frac{2\gamma}{\xi_1 P_v + \xi_2 C K_H - P_c^L} \qquad (4\text{-}44)$$

Briefly summarizing, for an equilibrium gas-vapor bubble subjected to a centrifugal field, the radius of curvature, 'h', at the center of the system is the basic parameter characterizing the equilibrium size and shape. For the special case of a dilute solution of a gas in a liquid, the introduction of a reference condition valid

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[4] The characteristic time scale for the diffusion process is of the order of

$$\tau_D \sim \frac{\ell^2}{D_c}$$

where D_c is the diffusion coefficient of the dissolved gas. For a solution of air in water ($D_c \sim 2.0 \times 10^{-5}$ cm^2 sec^{-1} [48]) with ℓ equal to 15 cm, τ_D is of the order of 10^7 seconds, or about 3000 hours.

for liquid tensions enables 'h' to be expressed in terms of the properties of the dilute solution, i.e. T, C, P_o, and P_c^L. In practice, when the bubble is essentially spherical 'h' represents the critical radius.

In the next chapter, the expression developed for 'h' will be used to calculate the critical radius of a specific system.

CHAPTER 5

THE CRITICAL RADIUS OF A GAS-VAPOR BUBBLE IN A DILUTE SOLUTION OF AIR IN WATER AT NEGATIVE PRESSURES

The previous chapter treated the special case of a gas-vapor bubble in a dilute solution of a single gas in a liquid solvent at negative pressure. In practice when $e << 1$, the radius of curvature 'h' at the center represents the critical radius of the bubble. Equation (4-44) expresses 'h' as a function of the properties of the dilute solution. Consider now the application of the expression for 'h' to a specific system containing a dilute solution of air in water at constant temperature.[1] Although air is a mixture of primarily two gases, it is commonly treated as a single gas component of fixed ratio, i.e. twenty-one per cent oxygen and seventy-nine per cent nitrogen.

Before proceeding to evaluate 'h' for the case of air in water, consider the range of validity of 'h', the approximation for the critical radius. As the bubble tends to a spherical shape, the ratio of the maximum radius, 'a', to the radius of curvature, 'h', at the center approaches

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[1] Air in water is a common example of a dilute solution of a "gas" in a liquid for which an abundance of data exists. The values of the properties of the system used in the evaluation of 'h' are recorded in Appendix C.

unity. Equation (2.2-14) can be rearranged to give

$$\frac{a}{h} = 1 + f\left(\frac{a}{h}\right)^3 \qquad (5\text{-}1)$$

where

$$f \equiv \frac{\rho^L \omega^2 h^3}{8\gamma} \qquad (5\text{-}2)$$

Figure 5-1 illustrates the deviation of the ratio $\frac{a}{h}$ from unity as a function of the parameter 'f'. Once 'h' is known, the value of 'f' follows from equation (5-2). For $f \ll 1$ in Figure 5-1, the deviation of $\frac{a}{h}$ from unity is approximately equal to 'f'. As $\frac{a}{h}$ approaches unity, 'f' becomes approximately equal to the shape parameter 'e'. Then for $f << 1$, i.e. $e << 1$, the difference between 'a' and 'h' is negligible, and the value of 'h' represents the critical radius of the bubble.

Equation (4-44) expresses 'h' as a function of four variables, namely the temperature, concentration, reference pressure, and the pressure at the center of the system in the dilute solution. The variable P_c^L represents the pressure outside the bubble at the center, which can be positive or negative. For the case of positive pressures, Ward et al. [49] expressed the critical radius as a function of the temperature, concentration, and pressure in the dilute solution. At zero angular velocity, where P_c^L is equal to P_o, expression (4-44) for 'h' reduces to that of Ward et al.

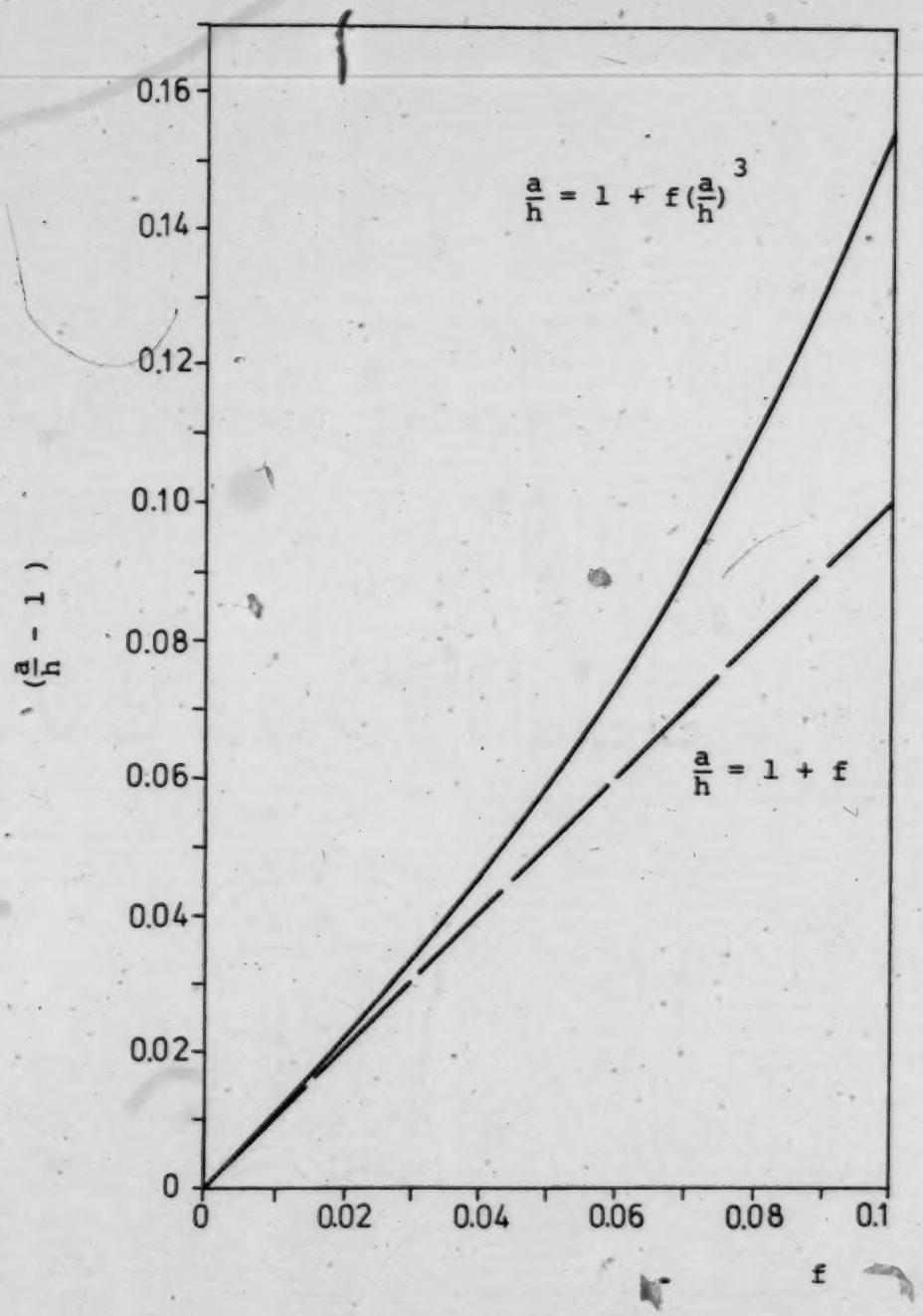

Figure 5-1 Deviation of the Gas-Vapor Bubble From Sphericity. $\frac{a}{h}$ is the ratio of the maximum radius to the radius of curvature at the center; f is the parameter $\frac{\rho L \omega^2 h^3}{8\gamma}$

When the system is rotating, the pressure difference $P_c^L - P_o$ in the ξ_2 term in expression (4-43) can be related to the angular velocity by equation (4-4). Thus, the additional variable P_o in the expression for the critical radius is a result of the pressure variation in the dilute solution due to the angular rotation.

In presenting the results, the variation of 'h' with P_c^L, C, and T will be examined, since these variables are thermodynamic properties of the liquid phase at the center of the system. However, first the dependence of 'h' on P_o must be determined. The reference pressure only appears in the exponential factor ξ_2 in equation (4-44) for 'h'. From equation (4-38), the term $\xi_2 CK_H$ physically represents the increase in pressure inside the bubble due to the presence of the solute in the system.

The variation of 'h' with P_o is presented in Figures 5-2a, 5-2b, and 5-2c as a function of P_c^L, C, and T, respectively. Figure 5-2a illustrates the effect of P_c^L on the dependence of 'h' on P_o for constant C and T. The change in 'h' with P_o only becomes appreciable as P_c^L becomes positive, and near the upper limit considered for P_o. Physically, the effect of P_o is negligible when the pressure outside the bubble is much greater in magnitude than that inside.

Next, consider the effect of C on the variation of 'h' with P_o for constant P_c^L and T. In Figure 5-2b the

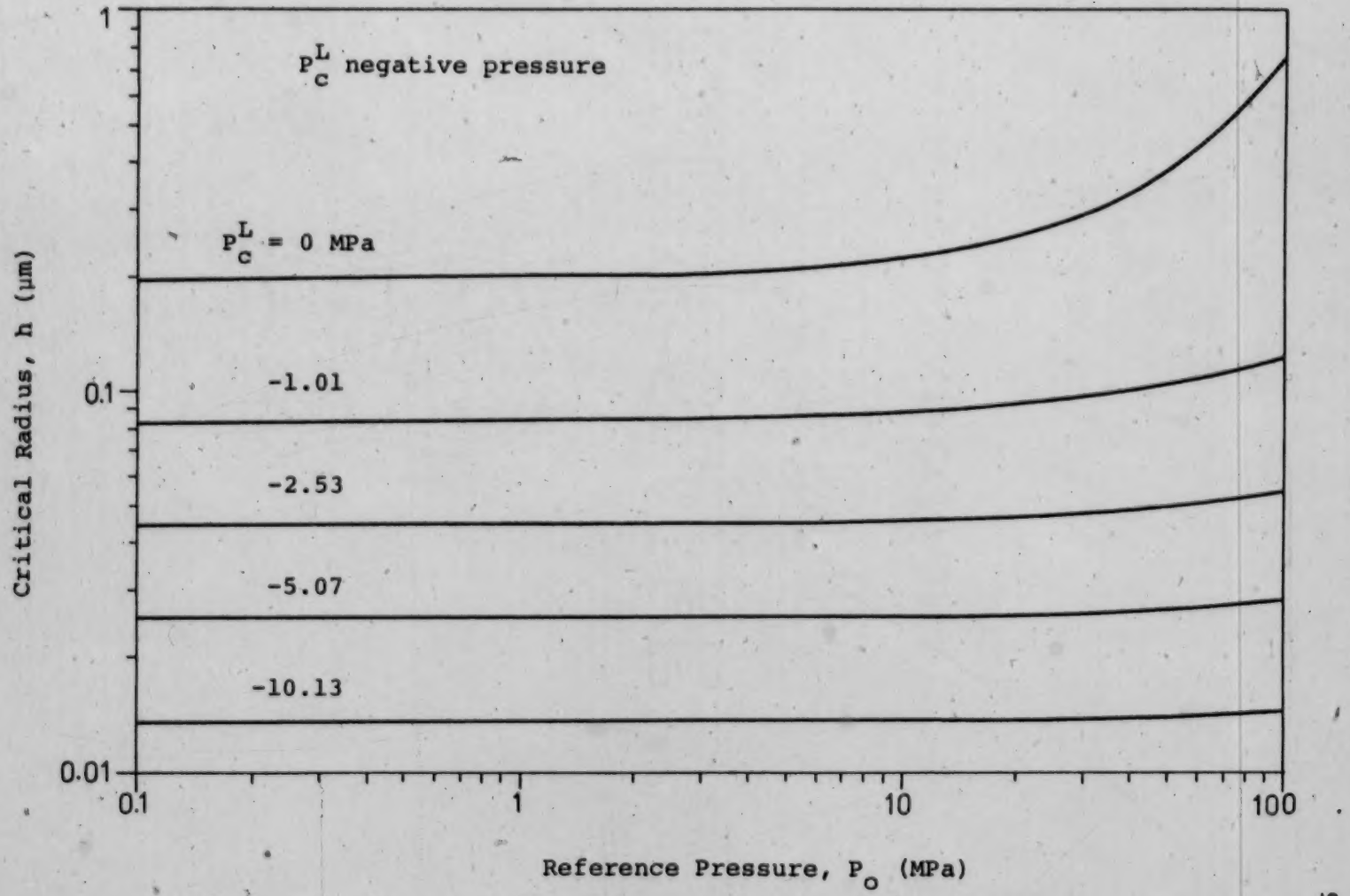

Figure 5-2a. Theoretical Results for the Dependence of the Critical Radius on the Reference Pressure at Various Negative Pressures. For a solution of air in water at a concentration of 10^{-4} and a temperature of 25°C

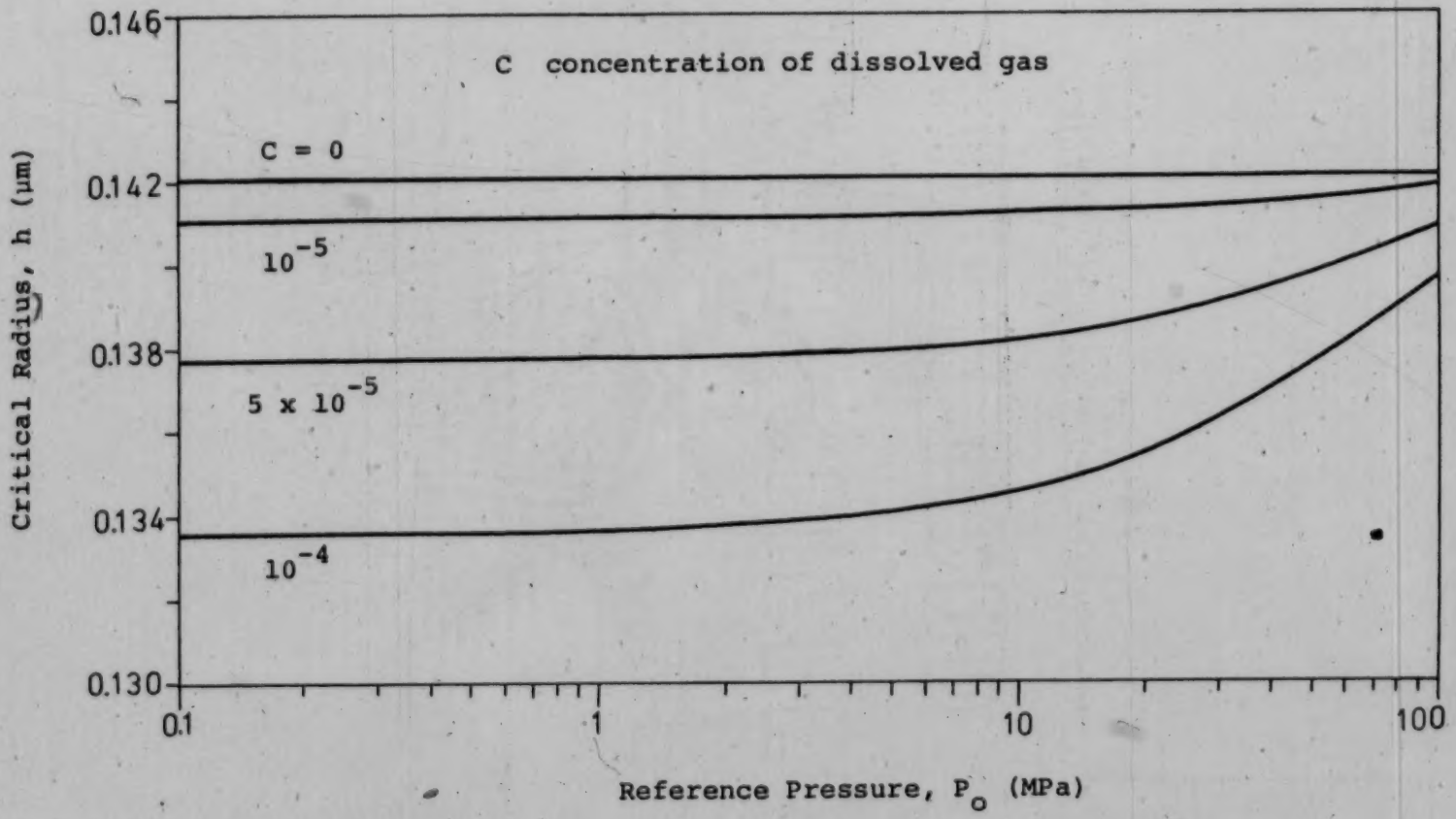

Figure 5-2b Theoretical Results for the Dependence of the Critical Radius on the Reference Pressure at Various Concentrations. For a solution of air in water at a negative pressure, P_c^L, of -10.13 MPa and a temperature of 25°C

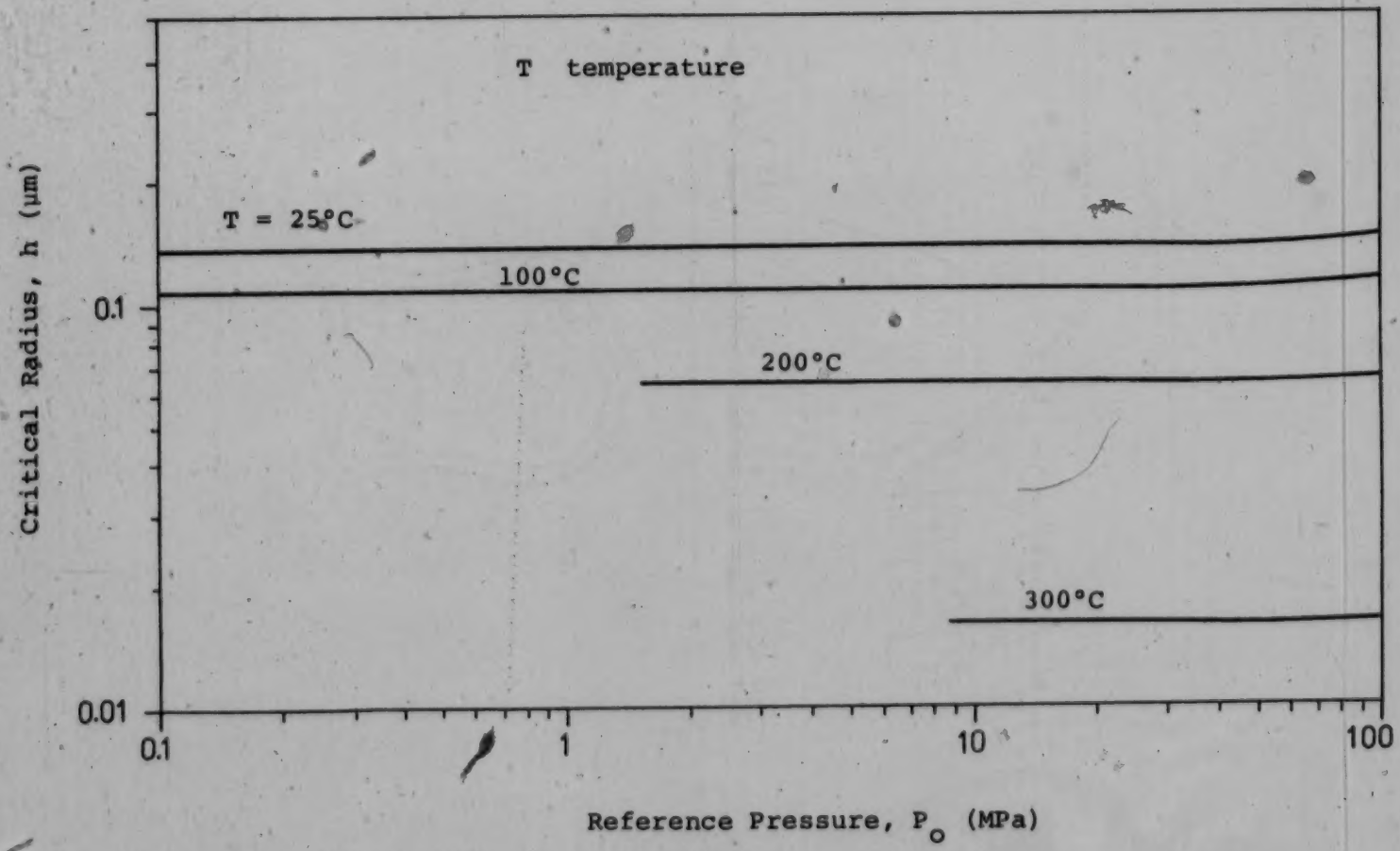

Figure 5-2c Theoretical Results for the Dependence of the Critical Radius on the Reference Pressure at Various Temperatures. For a solution of air in water at a negative pressure, P_c^L, of -10.13 MPa and a concentration of 10^{-4}

change in 'h' with P_o increases with C. This is evident from equation (4-44) where the relative magnitude of the partial pressure of the gas, i.e. $\xi_2 CK_H$, in comparison to the other pressure terms in the denominator determines the significance of P_o. As C goes to zero, the effect of P_o disappears. The reason the curves collapse onto the pure vapor limit is that for a given value of P_o the difference $P_c^L - P_o$ becomes increasingly large and negative as P_o increases, tending to cause ξ_2 to go to zero. The maximum change in 'h' is less than seven per cent over the entire range of P_o.

Finally, the effect of T on the change in 'h' with P_o at constant P_c^L and C is presented in Figure 5-2c. The value of 'h' for a given temperature is almost constant. Since K_H reaches a maximum around 100°C, the partial pressure of the gas and hence the effect of P_o is greatest at temperatures around 100°C. Even then, the change in 'h' with P_o is only perceptible near the upper limit of P_o considered.

Summarizing the results above, the effect of P_o on 'h' is negligible over a wide range of values of P_o, especially for large negative pressures. Since 'h' is independent of P_o, the critical radius can be considered a function of P_c^L, C, and T. The value of P_o used for computational purposes will be the equilibrium pressure of a gas-vapor mixture over a flat interface of a dilute solution at temperature T and concentration C. Then, P_o is expressed by

the relation [50]

$$P_o = \eta P_v + C K_H \qquad (5\text{-}3)$$

where

$$\eta \equiv \exp\left[\frac{v^L}{kT}(P_o - P_v) - C\right] \qquad (5\text{-}4)$$

Experimentally, this value of P_o corresponds to the pressure at which the liquid-gas solution is prepared. Since P_v and K_H depend on T, P_o is a function of T and C. However, since 'h' is independent of P_o over the range of P_o considered, the effect on 'h' of the change in P_o with T and C is negligible.

It should be noted that the choice of P_o given by equation (5-3) is equal to the pressure inside the bubble at zero angular velocity. Since the pressures inside and outside the bubble are then equal, the equilibrium interface for zero angular velocity has an infinite radius of curvature, i.e. is a flat surface. Thus, as P_c^L approaches the value of P_o given by equation (5-3), the critical radius tends to infinity, since the denominator in equation (4-44) approaches zero.

Having established the value of P_o to be used, the dependence of 'h' on P_c^L, C, and T can now be investigated. The variation of 'h' with P_c^L for several values of C and T is presented in Figures 5-3a to 5-3d. The value of 'h' decreases as the magnitude of the negative pressure P_c^L

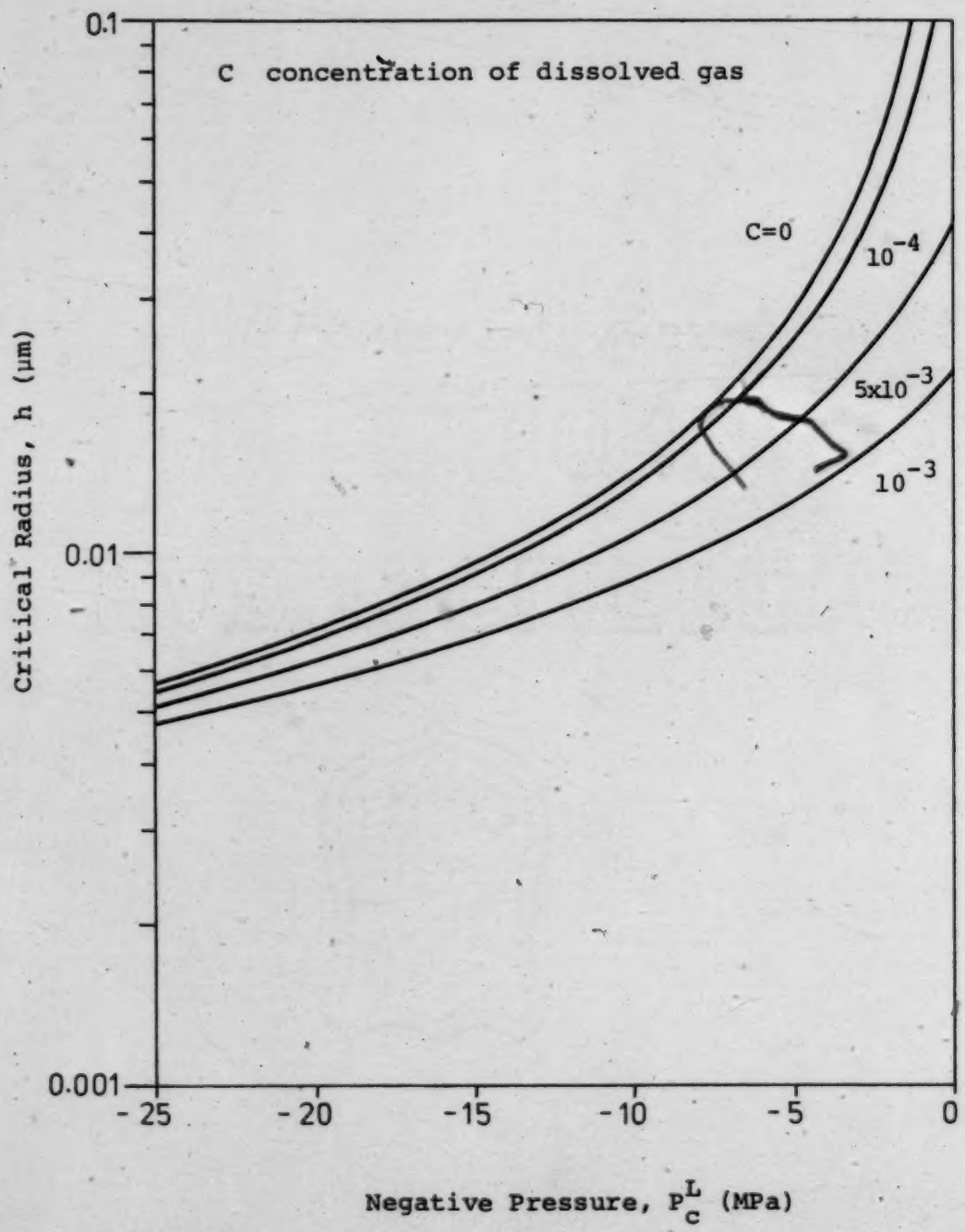

Figure 5-3a Theoretical Results for the Dependence of the Critical Radius on Negative Pressure at Various Concentrations. For a solution of air in water at a temperature of 25°C

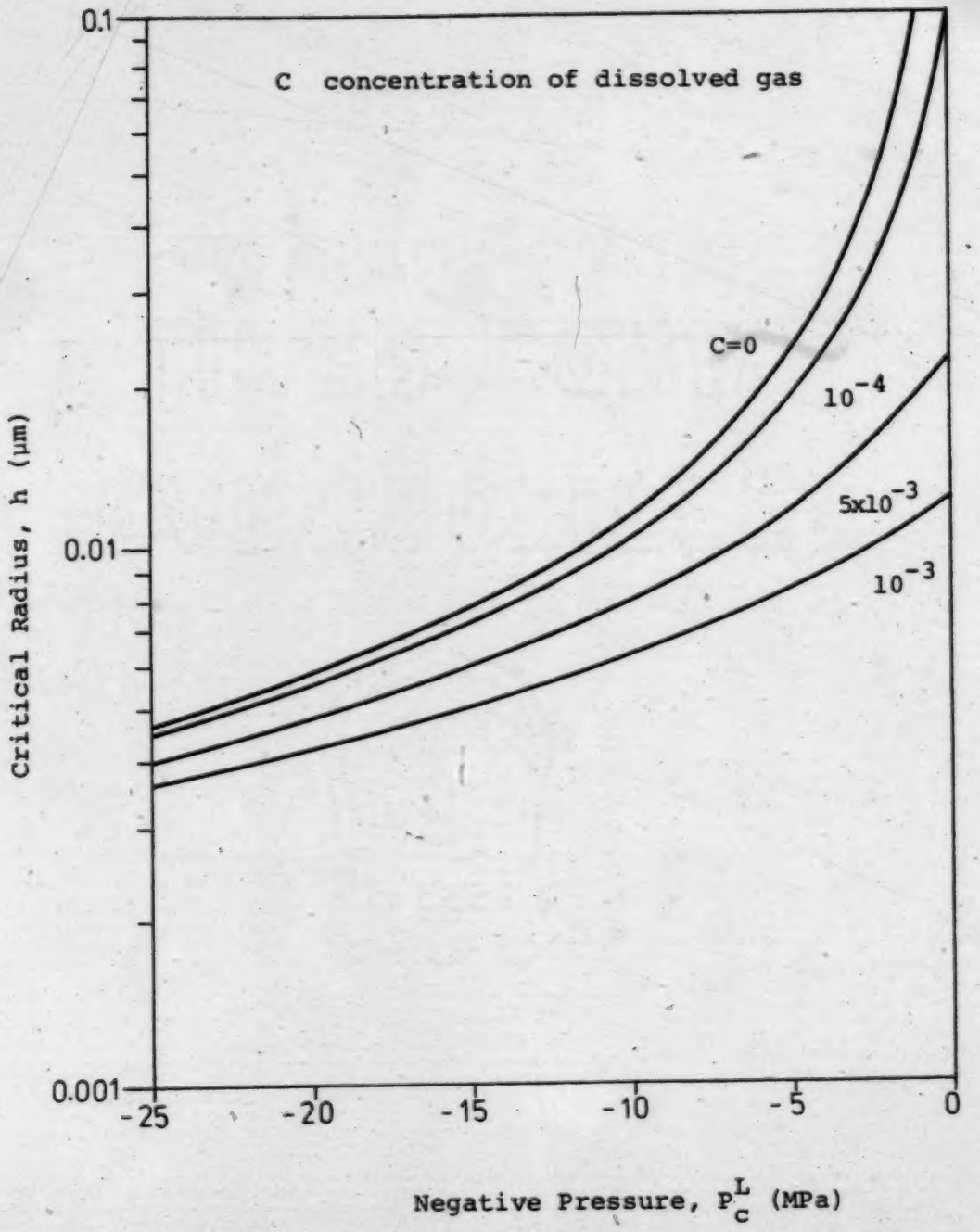

Figure 5-3b Theoretical Results for the Dependence of the Critical Radius on Negative Pressure at Various Concentrations. For a solution of air in water at a temperature of 100°C

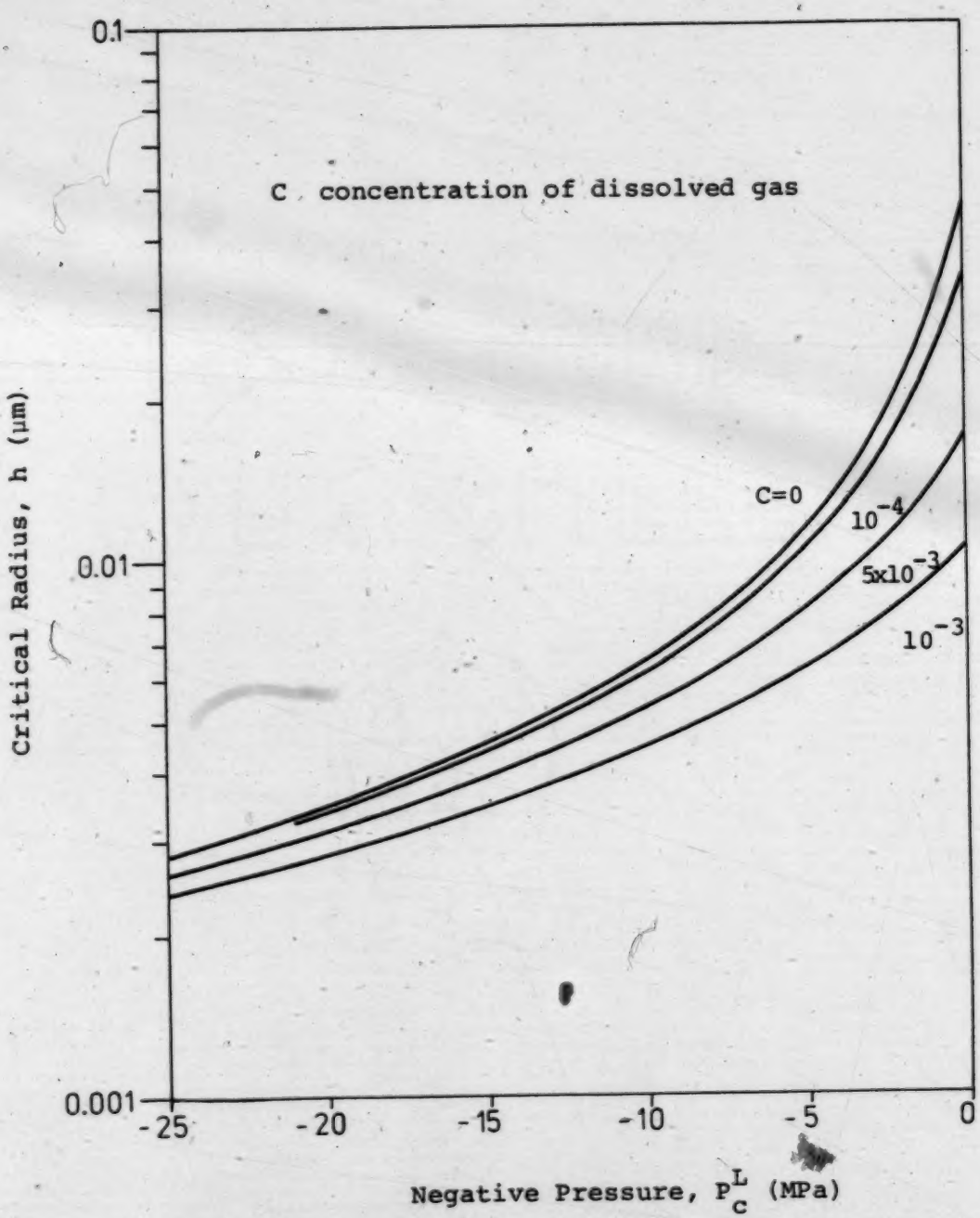

Figure 5-3c Theoretical Results for the Dependence of the Critical Radius on Negative Pressure at Various Concentrations. For a solution of air in water at a temperature of 200°C

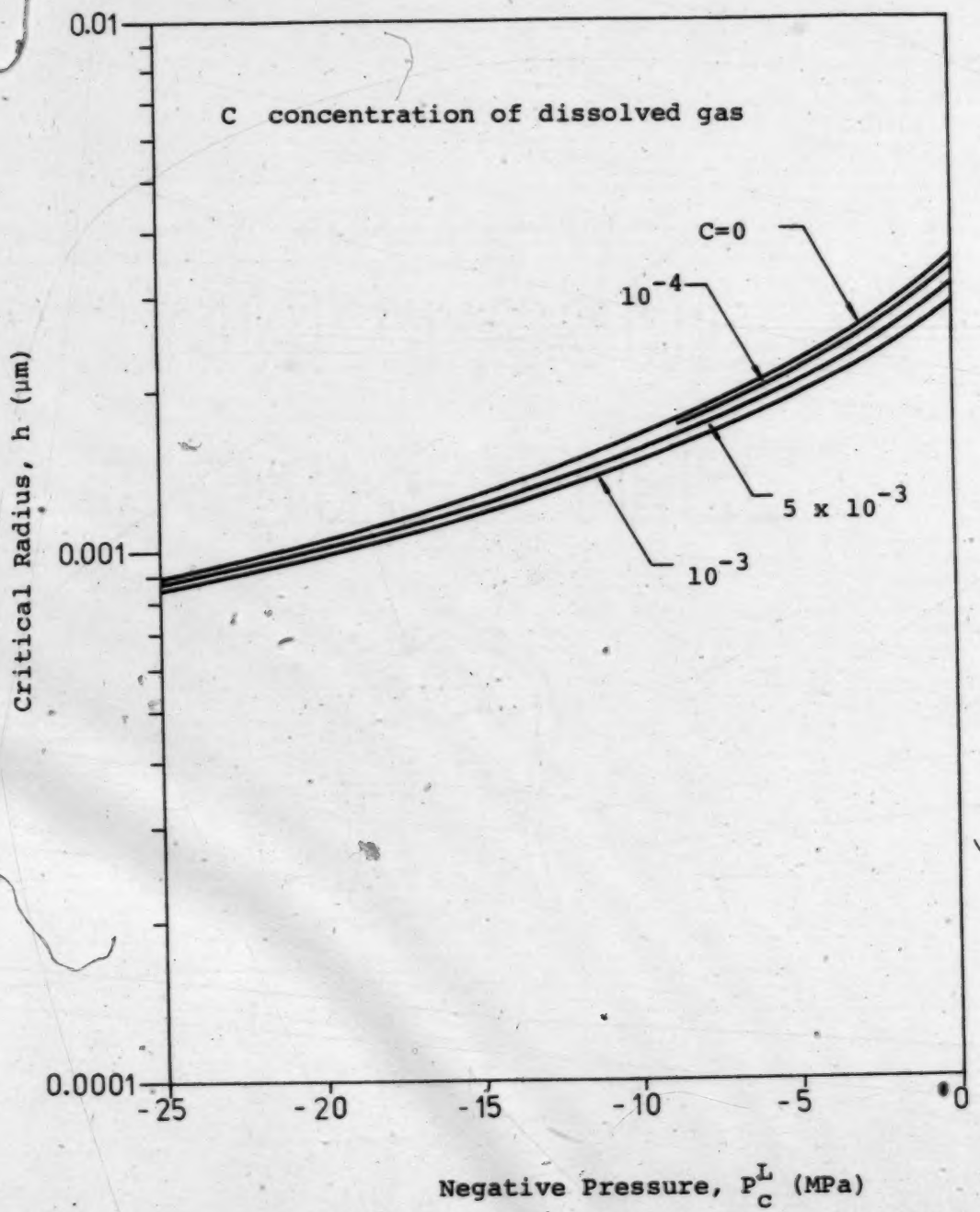

Figure 5-3d Theoretical Results for the Dependence of the Critical Radius on Negative Pressure at Various Concentrations. For a solution of air in water at a temperature of 300°C

increases. In equation (4-4), as P_c^L becomes large and negative, the pressure difference across the interface steadily increases, causing the critical radius to decrease. The rate of change of 'h' with P_c^L increases as P_c^L becomes positive. The value of 'h' tends to infinity as the pressure in the liquid tends to the value P_o.

Figures 5-3a to 5-3d also illustrate the effect of the solute concentration on the critical radius. At constant P_c^L and T, the value of 'h' decreases as C increases. For P_c^L large and negative, only high concentration levels appreciably reduce the value of 'h'. However, the effect of C on 'h' increases as P_c^L becomes positive.

The effect of increasing C is to increase the partial pressure of the gas inside the bubble, thus increasing the pressure difference across the bubble interface, and decreasing the critical radius. As P_c^L becomes smaller in magnitude, the significance of the partial pressure of the gas increases, and the curves for each concentration tend to diverge.

Comparing the spread of the curves in each of Figures 5-3a to 5-3d indicates that the dependence of the value of 'h' on C decreases with T. Since K_H decreases for temperatures above 100°C, the partial pressure of the gas also decreases with T. This explains the reduced effect of C on 'h' with T.

The results are summarized in Figure 5-4 which illustrates the change in 'h' with C at constant P_c^L and T. An upper bound of 10^{-3} has been used for C in order to better

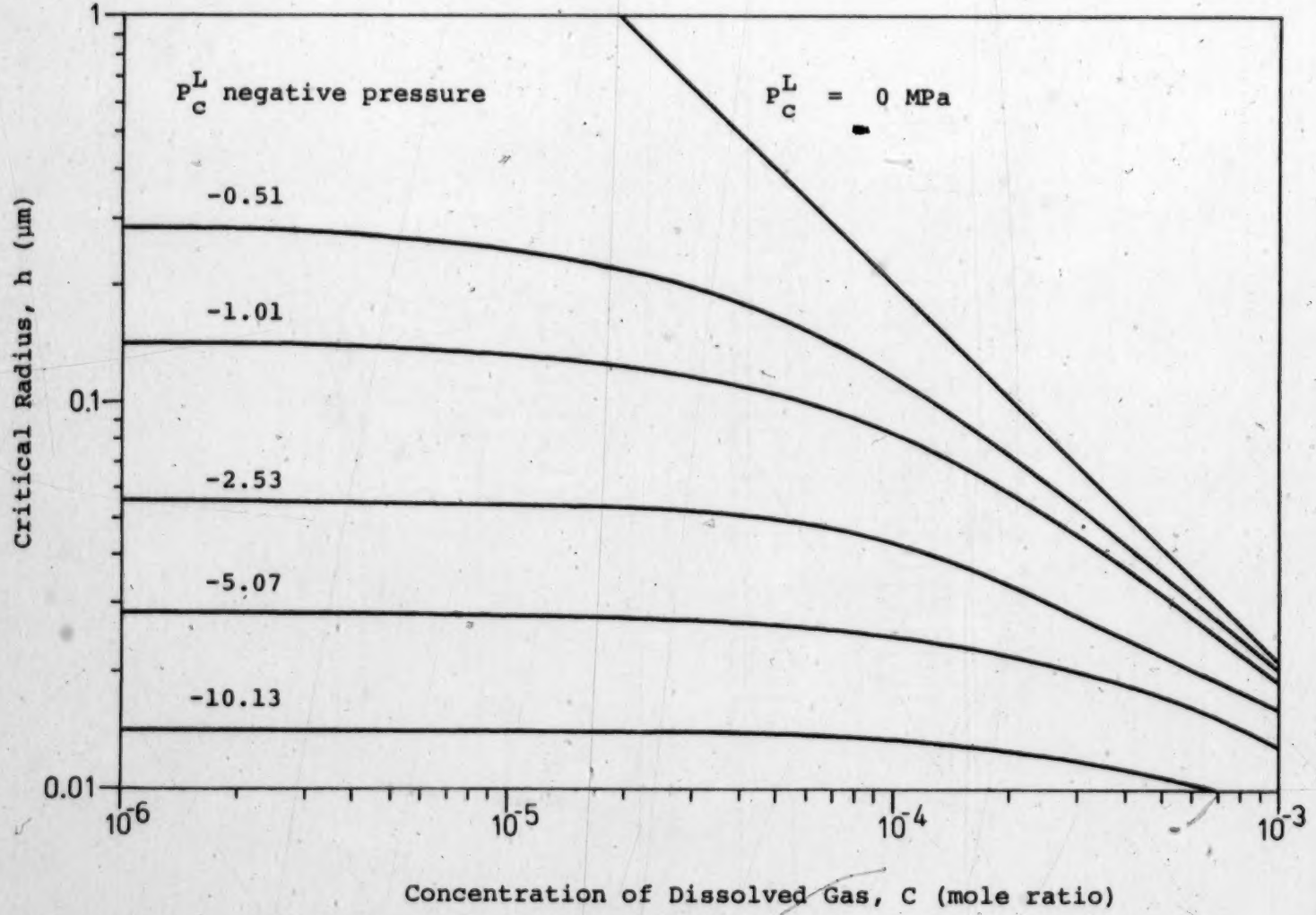

Figure 5-4 Theoretical Results for the Dependence of the Critical Radius on Dissolved Gas Content at Various Negative Pressures. For a solution of air in water at a temperature of 25°C

illustrate the effect of C on 'h', although this value is bordering on the upper limit for a dilute solution [51]. For C close to zero, the curves for negative values of P_c^L are almost horizontal. The exact magnitudes of the change in 'h' with C for these values are presented in Table 1.

The last effect to be considered is that of temperature on 'h' at constant P_c^L and C. In equation (4-44) the three properties which change significantly with T are the surface tension, vapor pressure, and Henry's law constant. Table 2 shows that γ decreases with T, while P_v increases. The value of K_H initially increases up to a maximum between 75°C and 100°C, and thereafter steadily decreases. The solubility has a minimum value at the maximum value of K_H.

The temperature variation of 'h' is illustrated in Figures 5-5a and 5-5b for the pure vapor case and a concentration of 10^{-3}, respectively. The pure vapor case represents an upper limit for 'h' at constant P_c^L and T. The temperature variation of 'h' for the pure vapor case depends only on the change in γ and P_v with T. From Figure 5-5a, the value of 'h' decreases with T for constant P_c^L. The rate of change of 'h' with T increases with temperature, and as P_c^L becomes positive, since the relative magnitude of P_v compared to P_c^L becomes larger.

The same general decrease in 'h' with temperature is shown in Figure 5-5b for a concentration of 10^{-3}. For a dilute solution, the temperature variation of 'h' depends

TABLE 1

THE DEPENDENCE OF THE CRITICAL RADIUS ON THE AIR CONTENT FOR WATER WITH VARIOUS NEGATIVE PRESSURES AT A TEMPERATURE OF 25°C

Dissolved Gas Content C (mole ratio)	Critical Radius, h (μm) Negative Pressure; P_c^L (MPa)				
	-10.13	-5.07	-2.53	-0.10	0.0
1×10^{-3}	0.00901	0.01272	0.01560	0.01891	0.02152
1×10^{-4}	0.01336	0.02503	0.04440	0.08288	0.3889
1×10^{-5}	0.01411	0.02802	0.05521	0.01322	1.873
1×10^{-6}	0.01419	0.02836	0.05660	0.1406	13.64
1×10^{-7}	0.01420	0.02839	0.05674	0.1415	36.75
0	0.01420	0.02840	0.05676	0.1416	45.28

TABLE 2

THE TEMPERATURE VARIATION OF THE SURFACE TENSION, VAPOR PRESSURE, AND HENRY'S LAW CONSTANT FOR A DILUTE SOLUTION OF AIR IN WATER

Temperature T (°C)	Surface Tension γ (N/m)	Vapor Pressure P_v (MPa)	Henry's Law Constant K_H (MPa)
0	0.07565	0.0006137	4357
25	0.07198	0.003179	7376
50	0.06795	0.01238	9612
75	0.06359	0.03868	10690
100	0.05892	0.1016	10701
125	0.05396	0.2328	9947
150	0.04875	0.4773	8756
175	0.04331	0.8946	7389
200	0.03768	1.558	6024
225	0.03191	2.556	4763
250	0.02605	3.986	3655
275	0.02017	5.961	2711
300	0.01437	8.609	1916

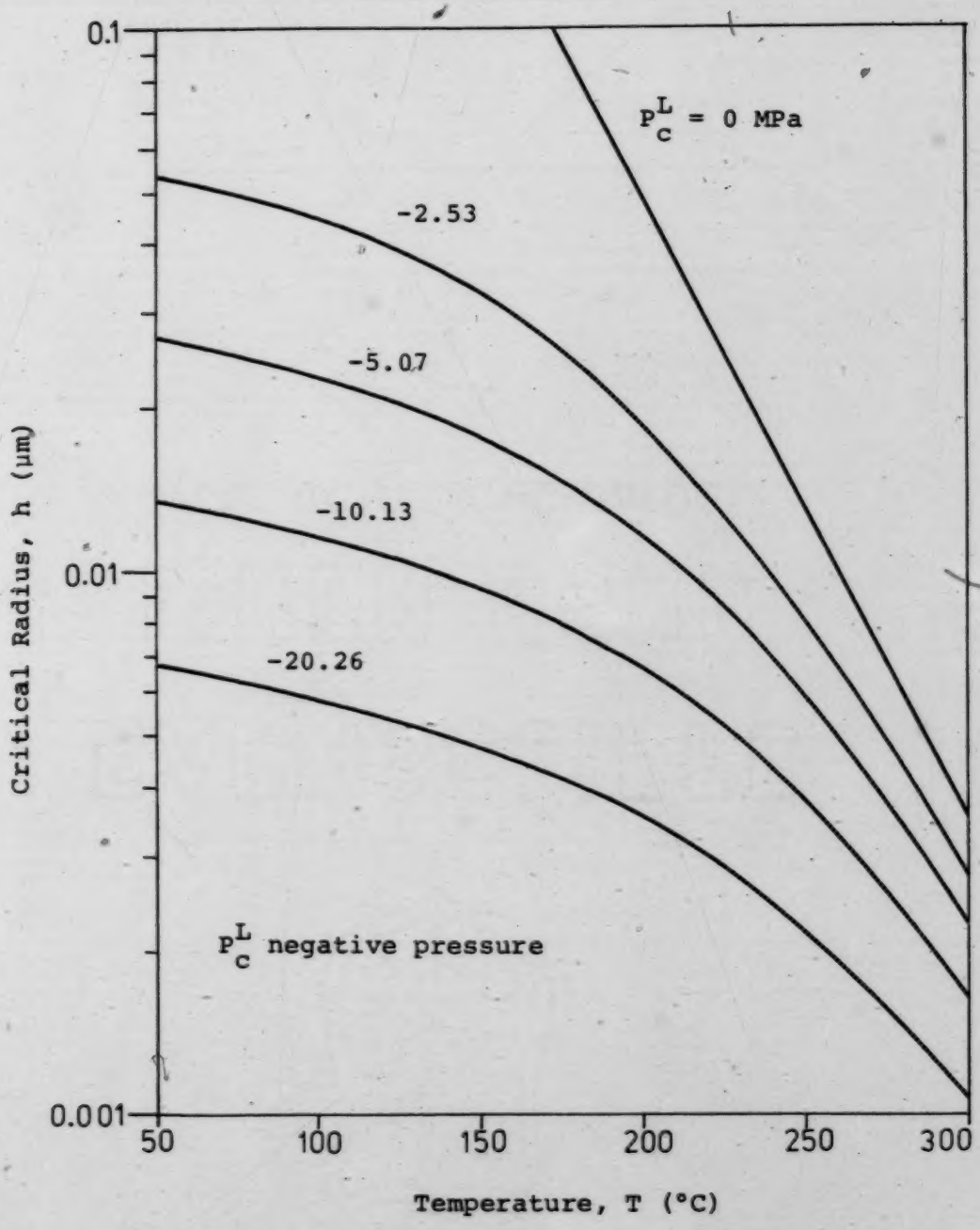

Figure 5-5a Theoretical Results for the Dependence of the Critical Radius on Temperature for a Pure Vapor Bubble in Water at Various Negative Pressures

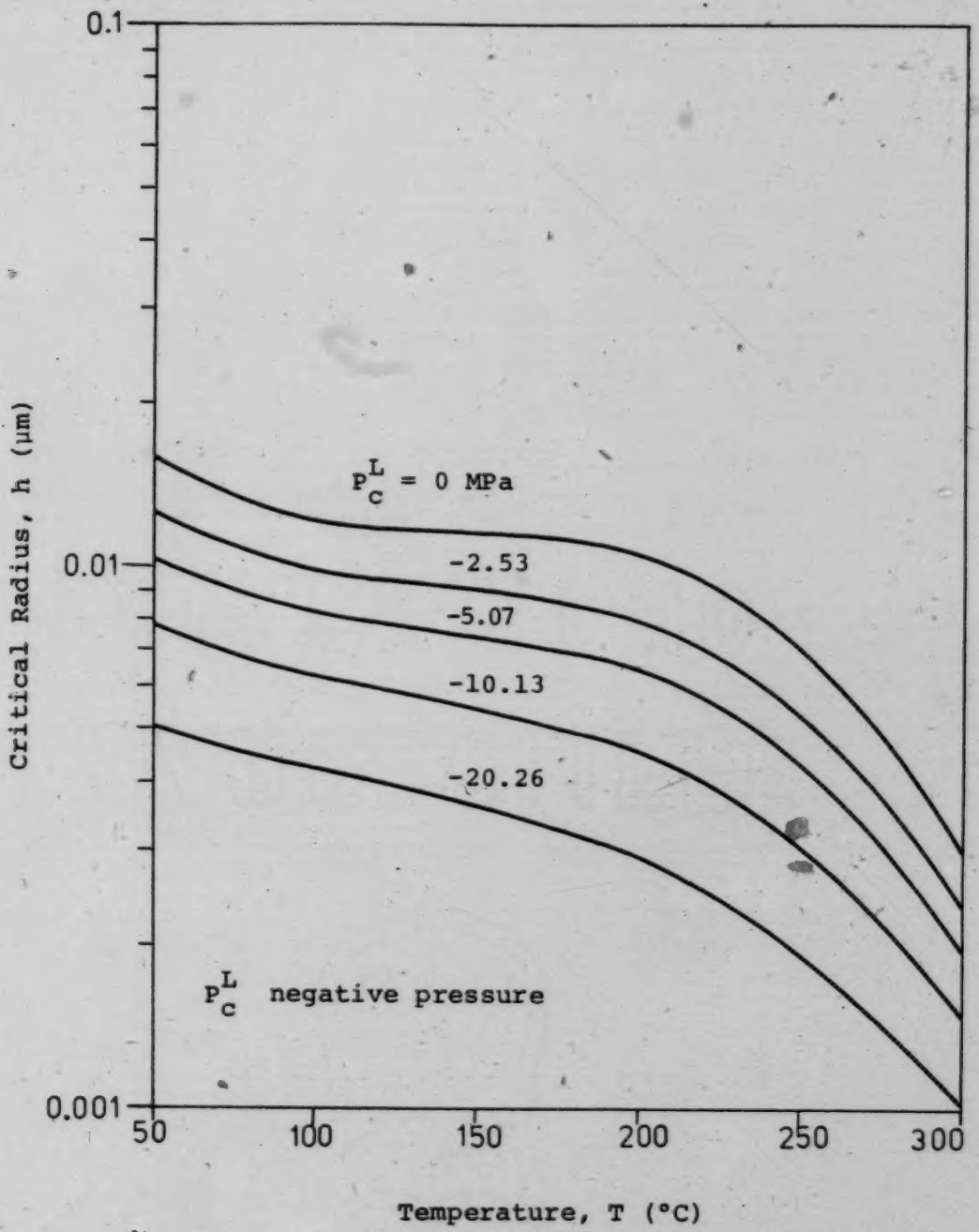

Figure 5-5b Theoretical Results for the Dependence of the Critical Radius on Temperature at Various Negative Pressures. For a solution of air in water at a concentration of 10^{-3}

upon the change in K_H with T, in addition to the change in γ and P_v. The relative variation of the magnitudes of the partial pressures of the vapor and gas inside the bubble due to the temperature variation of P_v and K_H introduces an inflection point in the curves of constant pressure in Figure 5-5b. The inflection point occurs around 100°C, at which temperature the value of K_H undergoes a maximum. As p_c^L becomes positive, the temperature variation of the partial pressures becomes more significant. In particular, the decrease in K_H tends to offset the temperature variation of 'h' with γ and P_v between 100°C and 200°C. For large temperatures, the effect of P_v dominates, reducing the value of 'h' sharply. The dependence of 'h' on the relative variation of the partial pressures becomes less and less as the magnitude of the negative pressure increases, since only the pressure difference across the interface is important.

The value of the critical radius at the critical temperature represents a lower limit for the temperature variation of 'h'. At the critical point for the liquid-gas solution,[2] the liquid and vapor phases become identical. Then, the interface between them ceases to exist, and the surface tension becomes equal to zero. Thus, the value of

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[2]The values of T_c and P_c for the dilute solution of air in water are not equal to the values for pure water, i.e. T_c = 374°C and P_c = 22.12 MPa [52]. In practice, a "mixing rule" is used to relate the value of T_c and P_c for the solution to the values of T_c and P_c for the pure solvent and solute [53].

the critical radius given by equation (4-44) is equal to zero at the critical point.

The value of 'h' is inversely proportional to the pressure difference across the bubble interface. The expressions in the denominator of equation (4-44) for the partial pressures of the gas-vapor mixture inside the bubble include the factors ξ_1 and ξ_2, given by expressions (4-39) and (4-43), respectively. These factors are functions of P_c^L, C, T, and P_o. Since the choice of P_o given by equation (5-3) is a function of C and T, it is sufficient to consider the variation with P_c^L, C, and T.

The exponential terms ξ_1 and ξ_2 represent reductions in the partial pressures of the vapor and gas inside the bubble due to the curvature of the interface. From equation (5-3), for a gas-vapor mixture in equilibrium with a dilute solution across a flat interface, the partial pressures of the vapor and gas are given respectively by

$$P_1^G = \eta P_v \qquad (5\text{-}5)$$

and

$$P_2^G = C K_H \qquad (5\text{-}6)$$

For η approximately equal to one[3], i.e. the partial pressure of the vapor approximately equal to the vapor pressure, the

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[3]For a dilute solution of air in water at a temperature of 25°C and a concentration of 10^{-4}, the value of η is 1.0053.

percentage reductions in the partial pressures of the vapor and gas due to the curvature of the interface become $(1 - \xi_1)$ and $(1 - \xi_2)$, respectively.

Table 3a illustrates the variation of $(1 - \xi_1)$ and $(1 - \xi_2)$ with P_c^L for constant C and T. Each value increases steadily as the magnitude of the negative pressure increases. The deviation of ξ_1 and ξ_2 from unity for large negative pressures significantly lowers the pressure inside the bubble in comparison to that for the case of a flat interface.

The variation of $(1 - \xi_1)$ and $(1 - \xi_2)$ with C at constant P_c^L and T is presented in Table 3b. The value of $(1 - \xi_1)$ is almost constant, while that of $(1 - \xi_2)$ decreases as C increases. In expression (4-39) for ξ_1, the effect of C is important only when P_c^L approaches P_v. In expression (4-43) for ξ_2, the only effect of C is to change P_o. This effect is negligible when the magnitude of P_c^L is much greater than P_o.

Finally, Table 3c considers the temperature variation of $(1 - \xi_1)$ and $(1 - \xi_2)$ for constant P_c^L and C. The values of $(1 - \xi_1)$ and $(1 - \xi_2)$ initially decrease to a minimum, and then increase with T, as a result of the temperature variation of v^L, P_v, and P_o, and the presence of T in the denominator of the exponents of both ξ_1 and ξ_2. The exact dependence of the percentage reductions in the partial pressures represented by $(1 - \xi_1)$ and $(1 - \xi_2)$ on both C and T is sensitive to the value of P_c^L. However, in general the

TABLE 3a

THE PERCENTAGE REDUCTIONS IN THE PARTIAL PRESSURES FOR VARIOUS NEGATIVE PRESSURES

(For a solution of air in water with a concentration of 10^{-4} and a temperature of 100°C)

Negative Pressure P_c^L (MPa)	Reduction in Partial Pressures	
	Vapor $1 - \xi_1$ (%)	Gas $1 - \xi_2$ (%)
0.0	0.072	1.239
-1.0	0.675	2.284
-2.5	1.573	3.831
-5.0	3.051	6.354
-7.5	4.507	8.812
-10.0	5.942	11.20
-25.0	14.11	24.30
-50.0	26.17	41.98
-75.0	36.54	55.52
-100.0	45.45	65.91

TABLE 3b

THE PERCENTAGE REDUCTIONS IN THE PARTIAL PRESSURES FOR VARIOUS CONCENTRATIONS

(For a solution of air in water with a negative pressure, P_c^L, of -10 MPa and a temperature of 100°C)

Concentration of Dissolved Gas C (mole ratio)	Reduction in Partial Pressure Vapor $1 - \xi_1$ (%)	Gas $1 - \xi_2$ (%)
1×10^{-3}	6.032	19.87
5×10^{-4}	5.985	15.17
1×10^{-4}	5.942	11.21
5×10^{-5}	5.938	10.70
1×10^{-5}	5.933	10.29
5×10^{-6}	5.933	10.24
1×10^{-6}	5.933	10.20

TABLE 3c

THE PERCENTAGE REDUCTIONS IN THE PARTIAL PRESSURES FOR VARIOUS TEMPERATURES

(For a solution of air in water with a negative pressure, P_c^L, of -10 MPa and a concentration of 10^{-4})

Temperature T (°C)	Reduction in Partial Pressures	
	Vapor $1 - \xi_1$ (%)	Gas $1 - \xi_2$ (%)
50	6.573	12.61
100	5.942	11.21
150	5.688	10.10
200	5.942	9.702
250	6.995	10.32
300	9.404	12.21

variation of $(1 - \xi_1)$ and $(1 - \xi_2)$ with C and T is small compared to the variation with P_c^L.

Having obtained actual values for the critical radius using expression (4-44) for 'h', the validity of this approximation can now be determined. Recall that the value of 'h' for the pure vapor case represents an upper limit at a given P_c^L and T. Then, from Figure 5-5a, it is evident that for P_c^L less than -5.0 MPa, 'h' is always less than 0.1 μm. Using this value of 'h' in equation (5-2) gives a value of 2×10^{-12} for 'f' at a temperature of 25°C and an angular velocity of 1000 rad/sec. From Figure 5-1, the deviation of $\frac{a}{h}$ from unity is approximately equal to the value of 'f', 2×10^{-12}. Since this deviation can be considered negligible, the bubble is essentially spherical of radius 'h'.

In summary, using expression (4-44) for 'h', the critical radius was evaluated for a dilute solution of air in water. Since 'h' is insensitive to P_o, the critical radius is essentially a function of P_c^L, C, and T. The value of 'h' decreases as the magnitude of the negative pressure in the solution outside the bubble increases. Increasing the solute concentration decreases the value of 'h'. Finally, 'h' decreases significantly at negative pressures as the temperature increases. In the region of negative pressures the bubble is essentially spherical.

CHAPTER 6

SUMMARY AND CONCLUSIONS

In the beginning of this investigation the concept of a critical size gas-vapor bubble was introduced to explain the phase transition of a liquid-gas solution to a gas-vapor mixture. Homogeneous nucleation theory postulates the creation of minute gas-vapor nuclei by fluctuations in the density of the liquid-gas solution. The reversible work required to form a critical size nucleus represents a type of "potential barrier" to the transition of the liquid-gas solution to a gas-vapor mixture [54]. If a bubble smaller than the critical size is formed, it spontaneously decays. If a bubble larger than the critical size is formed, it spontaneously grows, becoming a center for the formation of the new phase. Thus, the idea of a critical size nucleus is central to homogeneous nucleation theory.

For the case of positive pressure in the solution, the bubble is spherical, and the critical radius has previously been determined. However, a solution can be in a metastable state at negative pressures, i.e. the solution can be in tension. The purpose of this investigation is to determine the critical size of a gas-vapor bubble for the case of a solution at negative pressure.

The thermodynamic system considered corresponds to that used in practice to measure the tensile strengths of liquids by means of a centrifugal field. The gas-vapor bubble is imagined to exist at the center of rotation of a narrow tube filled with a liquid-gas solution. If the tube is rotated with sufficient angular velocity, the liquid outside the bubble at the center of the system can be placed in a state of tension.

The critical size and shape of the equilibrium bubble follow from the conditions of thermodynamic equilibrium. A plane section through the axis of rotation of the bubble can be approximated for negative pressure by the ellipse given by

$$\frac{x^2}{(1+e)^2 a^2} + \frac{r^2}{a^2} = 1 \qquad (6\text{-}1)$$

where 'a' is the maximum radius of the bubble, and 'e' is a shape parameter defined by equation (2.2-15). The magnitude of 'e' determines the deviation of the bubble from sphericity. For all practical purposes, at negative pressures the magnitude of 'e' is negligible, which implies that the bubble is essentially spherical.

The equilibrium state of the system is an unstable equilibrium, since the free energy of the bubble is a maximum. Thus, the equilibrium size of the bubble represents a critical value. A smaller bubble will spontaneously

collapse, while a larger bubble will spontaneously expand. A thermodynamic fluctuation in the density of the solution which produces a bubble larger than the critical size will initiate the formation of a gas-vapor filled cavity. The reversible work required to form a critical size gas-vapor bubble is given by

$$W_R = \frac{4\pi \gamma a^2}{3} \qquad (6\text{-}2)$$

where for negative pressures the magnitude of 'e' is negligible.

The critical radius is closely approximated by the radius of curvature, 'h', at the center of the bubble, since the value of 'e' is very small. Thus, the critical radius can be represented by the expression for 'h' obtained from the equilibrium conditions. For the special case of a dilute solution of a gas in a liquid, the critical radius can be expressed in terms of the properties of the dilute solution. Introducing an appropriate reference condition valid for negative pressures in the dilute solution outside the bubble results in

$$h = \frac{2\gamma}{\xi_1 P_v + \xi_2 C K_H - P_c^L} \qquad (6\text{-}3)$$

where ξ_1 and ξ_2 are exponential terms which deviate from unity, and are expressed by equations (4-39) and (4-43), respectively.

Using equation (6-3) for 'h', the critical radius was evaluated for the specific case of a dilute solution of air in water. The critical radius was essentially a function of the temperature, concentration, and pressure of the liquid phase at the center of the system, being independent of the reference pressure. As the magnitude of the negative pressure increased, the value of the critical radius decreased. The effect of the solute was to reduce the bubble size, although a significant reduction was only effected by concentrations near the upper limit for a dilute solution. The dependence of the critical radius on the temperature followed from the variation of the surface tension, vapor pressure, and Henry's law constant with temperature.

The dependence of the expression for the critical radius given by (6-3) on the solution properties outside the bubble has several implications for the tensile strength of a dilute solution in a centrifugal system. These implications assume that the liquid fracture occurs in the body of the fluid, i.e. not at a surface, and that homogeneous nucleation is the mechanism responsible for the formation of the gas-vapor cavity precipitating liquid fracture. As the magnitude of the negative pressure in the solution at the center increases, the value of the critical radius steadily decreases. The reversible work required to form the critical nucleus decreases as the critical radius becomes smaller. However, as the reversible work decreases, the probability of the

formation of a critical size gas-vapor nucleus increases, since the probability is proportional to the negative exponential of the reversible work. At some point, the formation of a nucleus greater than critical size becomes reasonably likely over a short period of time. When this negative pressure is reached, the liquid at the center would be expected to rupture. This negative pressure represents the tensile limit of the liquid solution.

The fact that increasing the concentration of the gas does not significantly reduce the critical radius except at large concentration levels implies that for a dilute solution the tensile strength is not substantially reduced by the presence of dissolved gas. Since there is no general concensus as to the effect of dissolved gas on the experimentally determined tensile strengths of liquids, the validity of this implication cannot at present be confirmed.

The temperature dependence of the critical radius suggests that the tensile strength of a liquid-gas solution is significantly reduced as the temperature of the system increases. Although there has been both experimental and theoretical work which seems to bear this out [55], there is a notable lack of data from a centrifugal system at high temperatures.

This investigation considered the equilibrium size and shape of a gas-vapor bubble in a liquid-gas solution subject to a centrifugal field. The radial pressure

distribution in the solution due to the centrifugal field was used to generate tensions in the solution outside the bubble. For the small, equilibrium gas-vapor bubbles corresponding to negative pressures in the liquid-gas solution, the bubble shape is approximately spherical. For such a bubble in a dilute, liquid-gas solution, the critical radius is a function of the properties of the liquid phase outside the center of the bubble. Since the equilibrium size of the gas-vapor bubble is very small, any direct observation of the equilibrium size and shape would be impossible. However, the expression for the critical radius can be used to obtain theoretical predictions for the tensile strengths of dilute, liquid-gas solutions in a centrifugal system on the basis of homogeneous nucleation theory. The comparison of these predictions with experimentally determined values would provide a means of indirectly verifying the results obtained in this investigation.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Knapp, R.T., Daily, J.W., and Hammitt, F.G., "Cavitation", McGraw-Hill, New York, 1970, p. 1.

2. Plesset, M.S., "The Tensile Strength of Liquids", Cavitation State of Knowledge, ASME, 1969, p. 15.

3. Fischer, J.C., "The Fracture of Liquids", J. Appl. Phys., 19, 1948, p. 1064.

4. Holl, J.W., "Nuclei and Cavitation", Trans. ASME, J. Basic Eng., 92, Dec. 1970, p. 681.

5. Knapp, R.T. et al., op. cit., p. 62.

6. Frenkel, J., "Kinetic Theory of Liquids", Dover, New York, 1955, pp. 366-381.

7. Landau, L.D., and Lifshitz, E.M., "Statistical Physics", Pergamon, Oxford, 2nd ed., 1968, pp. 471-474.

8. Callen, H.B., "Thermodynamics", Wiley, New York, 1960, pp. 267-272.

9. Landau, L.D., and Lifshitz, E.M., op. cit., p. 349.

10. Ward, C.A., Balakrishnan, A., and Hooper, F.C., "On the Thermodynamics of Nucleation in Weak Gas-Liquid Solutions", Trans. ASME, J. Basic Eng., 92, Dec. 1970, pp. 695-701.

11. Blake, F.G., Jr., "The Tensile Strength of Liquids: A Review of the Literature", Tech. Memo. No. 9, Acoustics Res. Lab., Harvard Univ., June 11, 1949.

12. Galloway, W., "An Experimental Study of Acoustically Induced Cavitation in Liquids", J. Acoust. Soc. Am., 26, 1954, pp. 849-857.

13. Briggs, L., "Limiting Negative Pressure of Water", J. Appl. Phys., 21, 1950, pp. 721-722.

14. Reynolds, O., "On the Internal Cohesion of Liquids and the Suspension of a Column of Mercury to a Height of More Than Double That of the Barometer", Mem. Manch. Lit. Phil. Soc., 7, Ser. 3, 1882, pp. 1-19.

15. Temperley, H.N.V., and Chambers, LL.G., "The Behaviour of Water Under Hydrostatic Tension: I", Proc. Phys. Soc. (London), 58, 1946, pp. 420-436.

16. Apfel, R.E., and Smith, M.P., Jr., "The Tensile Strength of Di-ethyl Ether Using Briggs's Method", J. Appl. Phys., 48, 1977, pp. 2077-2078.

17. Donoghue, J.J., Vollrath, R.E., and Gerjuoy, E., "The Tensile Strength of Benzene", J. Chem. Phys., 19, 1951, pp. 55-61.

18. Hammitt, F.G., "Effects of Gas Content Upon Cavitation Inception, Performance, and Damage", Report No. UMICH 01357-19-T, Cavitation and Multiphase Flow Lab., Univ. of Michigan, 1971, p. 20.

19. Iyengar, K.S., and Richardson, E.G., "The Role of Cavitation Nuclei", Fluids Report No. 57, Mech. Engr. Res. Lab., Fluid Mech. Div., August, 1957.

20. Kuper, C.G., and Trevena, D.H., "The Effect of Dissolved Gases on the Tensile Strength of Liquids", Proc. Phys. Soc. (London), 65, 1952, pp. 46-54.

21. Harvey, E.N. et al., "Bubble Formation in Animals II", J. Cell. Comp. Physiol., 24, 1944, pp. 23-27.

22. Rayleigh, Lord, "The Equilibrium of Revolving Liquid Under Capillary Force", Phil. Mag., 28, 1914, pp. 161-170.

23. Rosenthal, D.K., "The Shape and Stability of a Bubble at the Axis of a Rotating Liquid", J. Fluid Mech., 12, 1962, pp. 358-363.

24. Princen, H.M., Zia, I.Y.Z., and Mason, S.G., "Measurement of Interfacial Tension from the Shape of a Rotating Drop", J. Coll. Int. Sci., 23, 1967, pp. 99-107.

25. Callen, H.B., op. cit., p. 105.

26. Gibbs, J.W., "The Scientific Papers of J. Willard Gibbs", Dover, New York, 1961, pp. 219-231.

27. Ibid., p. 227.

28. Ibid., p. 229.

29. Ibid., pp. 276-285.

30. Defay, R., Prigogine, I., and Bellemans, A., "Surface Tension and Adsorption", Wiley, New York, 1966, pp. 87-88.

31. Kraus, H., "Thin Elastic Shells", Wiley, New York, 1967, p. 20.

32. Rayleigh, Lord, op. cit., p. 163.

33. Frenkel, J., op. cit., p. 374.

34. Daugherty, R.L., and Franzini, J.B., "Fluid Mechanics With Engineering Applications", McGraw-Hill, New York, 7th ed., 1977, p. 540.

35. Spiegel, M.R., "Mathematical Handbook of Formulas and Tables", Schaum's Outline Series, McGraw-Hill, New York, 1968, p. 110.

36. Callen, H.B., op. cit., pp. 131-145.

37. Glansdorf, P., and Prigogine, I., "Thermodynamic Theory of Structure, Stability, and Fluctuations", Wiley, London, 1971, pp. 14-16.

38. Ward., C.A. et al., op. cit., p. 697.

39. Ibid., p. 696.

40. Landau, L.D., and Lifshitz, E.M., op. cit., p. 275.

41. Prigogine, I., and Defay, R., "Chemical Thermodynamics", Longmans Green, London, 1954, pp. 126-127.

42. Landau, L.D., and Lifshitz, E.M., op. cit., p. 277.

43. Andrews, F.C., "Thermodynamics: Principles and Applications", Wiley, New York, 1971, p. 162.

44. Ward, C.A. et al., op. cit., p. 697.

45. Callen, H.B., op. cit., pp. 99-100.

46. Prigogine, I., and Defay, R., op. cit., p. 334.

47. Briggs, L., op. cit., p. 721.

48. Bolz, R.E., and Tuve, G.L., eds., "CRC Handbook of Tables for Applied Engineering Science", The Chemical Rubber Co., Cleveland, 1970, p. 453.

49. Ward, C.A. et al., op. cit., p. 698.

50. Forest, T.W., and Ward, C.A., "Homogeneous Nucleation of Bubbles in Solutions at Pressures Above the Vapor Pressure of the Pure Liquid", J. Chem. Phys., 69, 1978, p. 2222.

51. Prausnitz, J.M., "Molecular Thermodynamics of Fluid-Phase Equilibria", Prentice-Hall, Englewood Cliffs, N.J., 1969, p. 354.

52. Meyer, C.A. et al., eds., "ASME Steam Tables: Thermodynamic and Transport Properties of Steam", ASME, New York, 3rd ed., 1967, p. 14.

53. Prausnitz, J.M., op. cit., p. 148.

54. Frenkel, J., op. cit., p. 375.

55. Knapp, R.T. et al., op. cit., pp. 55-56.

56. Princen, H.M. et al., op. cit., p. 101.

57. Gröbner, W., and Hofreiter, N., "Integraltafel", Springer-Verlag, Innsbruck, 1949, p. 78.

58. Spiegel, M.R., op. cit., p. 70.

59. Ibid., p. 111.

60. Ibid., p. 70.

61. Irvine, T.F., Jr., and Hartnett, J.P., eds., "Steam and Air Tables in S.I. Units", Hemisphere Publishing, Washington, 1976, pp. 2-13.

62. Meyer, C.A., et al., op. cit., p. 17.

63. Hildebrand, J.H., Prausnitz, J.M., and Scott, R.L., "Regular and Related Solutions", Van Nostrand Reinhold, New York, 1970, p. 137.

64. Prausnitz, J.M., op. cit., pp. 424-425.

65. Meyer, C.A. et al., op. cit., p. 80q.

66. Defay, R., Prigogine, I., and Bellemans, A., op. cit., pp. 170-171.

67. Himmelblau, D.M., and Arends, E., "Die Löslichkeit Inerter Gase in Wasser bie hohen Temperaturen und Drucken", Chem.-Ing.-Tech., 31, 1959, pp. 791-795.

APPENDICES

APPENDIX A

THE GENERAL EXPRESSION FOR THE EQUILIBRIUM SHAPE OF THE GAS-VAPOR BUBBLE

The solution to equation (2.2-22), i.e.

$$\frac{dX}{dR} = \frac{-R[(1+e) - eR^2]}{\{1 - R^2[(1+e) - eR^2]^2\}^{1/2}} \tag{A-1}$$

for the equilibrium shape of a gas-vapor bubble in a liquid-gas solution subject to a centrifugal field can be obtained in terms of elliptic integrals of the first and second kind.[1] Using the transformation

$$Y \equiv (1 + e) - eR^2 \tag{A-2}$$

where

$$dY = -2eRdR \tag{A-3}$$

in equation (A-1) results in

$$dX = \frac{YdY}{2e^{1/2}\,[Y^3 - (1+e)Y^2 + e]^{1/2}} \tag{A-4}$$

Integrating equation (A-4) gives

$$X = \frac{1}{2e^{1/2}} \int \frac{YdY}{W^{1/2}} + Q \tag{A-5}$$

---

[1] The method of solution closely follows that used by Princen et al. [56] in their treatment of a fluid bubble immersed in and rotating with a heavier fluid.

where

$$W \equiv Y^3 - (1 + e)Y^2 + e \qquad \text{(A-6)}$$

and Q is a constant of integration. The roots $Y_1 > Y_2 > Y_3$ of the cubic term W(Y) are given by

$$Y_1 = 1 \qquad \text{(A-7)}$$

$$Y_2 = \frac{1}{2} e + \sqrt{e(1 + \frac{e}{4})} \qquad \text{(A-8)}$$

$$Y_3 = \frac{1}{2} e - \sqrt{e(1 + \frac{e}{4})} \qquad \text{(A-9)}$$

For the interval $Y_1 \leq Y \leq 1+e$ corresponding to $0 \leq R \leq 1$, the use of the transformations

$$Y = \frac{Y_1 - Y_2 \sin^2 \Psi}{1 - \sin^2 \Psi} \qquad \text{(A-10)}$$

and

$$K^2 = \frac{Y_2 - Y_3}{Y_1 - Y_3} \qquad \text{(A-11)}$$

results in the following expression for the integral in equation (A-5) [57]:

$$\int \frac{Y dY}{W^{1/2}} = \frac{2}{\sqrt{(Y_1 - Y_3)}} [Y_1 F(K,\Psi) - (Y_1 - Y_3) E(K,\Psi) + (Y_1 - Y_3) \tan\Psi (1 - K^2 \sin^2\Psi)^{1/2}] \qquad \text{(A-12)}$$

where $F(K,\Psi)$ and $E(K,\Psi)$ are elliptic integrals of the first and second kind. Substituting expression (A-12) in (A-5) gives

$$X = \frac{1}{\sqrt{e(Y_1-Y_3)}} \left[Y_1 F(K,\Psi) - (Y_1 - Y_3) E(K,\Psi) + (Y_1 - Y_3) \tan\Psi (1 - K^2 \sin^2\Psi)^{1/2}\right] + Q \qquad \text{(A-13)}$$

The constant of integration can be determined by evaluating equation (A-13) at the point X=0 and R=1, where $Y=Y_1$. Equation (A-10) can be rearranged to give an expression for Ψ, i.e.

$$\Psi = \sin^{-1}\left[\left(\frac{Y - Y_1}{Y - Y_2}\right)^{1/2}\right] \qquad \text{(A-14)}$$

From equation (A-14) evaluated at $Y=Y_1$, $\Psi=0$. For $\Psi=0$, $\tan\Psi$, $F(K,\Psi)$, and $E(K,\Psi)$ are all equal to zero. Thus, equation (A-13) evaluated at X=0 and R=1 yields

$$Q = 0 \qquad \text{(A-15)}$$

Then, equation (A-13) for the equilibrium shape of a plane section through the axis of rotation of the gas-vapor bubble becomes

$$X = \frac{1}{\sqrt{e(Y_1 - Y_3)}} [Y_1 F(K,\Psi) - (Y_1 - Y_3)E(K,\Psi)$$

$$+ (Y_1 - Y_3) \tan\Psi (1 - K^2\sin^2\Psi)^{1/2}] \qquad (A-16)$$

APPENDIX B

DERIVATION OF EXPRESSIONS FOR THE SURFACE AREA, VOLUME, AND MOMENT OF INERTIA OF THE SPHEROID

For the case of negative pressures in the liquid-gas solution, when e << 1, the equilibrium shape of the gas-vapor bubble was approximated by the spheroid represented by equation (3-31), i.e.

$$\frac{x^2}{b^2} + \frac{r^2}{a^2} = 1 \qquad \text{(B-1)}$$

where

$$b \equiv (1 + e)\, a \qquad \text{(B-2)}$$

Expressions for the surface area, A, the volume, V, and the moment of inertia, I, of the spheroid will be obtained in terms of the maximum radius, 'a', and the shape parameter, 'e'.

B.1 Surface Area

If ds is the element of arc length of the curve given in Figure 2.2-1, the surface area can be expressed as

$$A = \int_A 2\pi r\, ds \qquad \text{(B.1-1)}$$

or using $ds = (\frac{ds}{dx})dx$,

$$A = 4\pi \int_0^b r\, (\frac{ds}{dx})\, dx \qquad \text{(B.1-2)}$$

From equation (B-1)

$$\frac{dr}{dx} = \frac{-ax}{b^2} \left(1 - \frac{x^2}{b^2}\right)^{-1/2} \qquad \text{(B.1-3)}$$

Elementary calculus gives the differential relationship expressed by

$$\frac{ds}{dx} = \left[1 + \left(\frac{dr}{dx}\right)^2\right]^{1/2} \qquad \text{(B.1-4)}$$

Using expression (B.1-3) in (B.1-4) results in

$$\frac{ds}{dx} = \frac{a}{r} \left(1 - \frac{B^2x^2}{b^2}\right)^{1/2} \qquad \text{(B.1-5)}$$

where the eccentricity, B, is defined by

$$B \equiv \left(1 - \frac{a^2}{b^2}\right)^{1/2} \qquad \text{(B.1-6)}$$

Substituting equation (B.1-5) back into (B.1-2), and rearranging terms yields the following expression for A:

$$A \equiv \frac{4\pi Ba}{b} \int_0^b \left(\frac{b^2}{B^2} - x^2\right)^{1/2} dx \qquad \text{(B.1-7)}$$

Using integral tables [58] to perform the integration in equation (B.1-7) results in

$$A = \frac{4\pi Ba}{b}\left[\frac{x}{2}\left(\frac{b^2}{B^2} - x^2\right)^{1/2} + \frac{b^2}{2B^2}\sin^{-1}\left(\frac{Bx}{b}\right)\right]_0^b \qquad \text{(B.1-8)}$$

or upon evaluating the limits,

$$A = 4\pi a\left[\frac{b}{2}\left(1 - B^2\right)^{1/2} + \frac{b}{2B}\sin^{-1}(B)\right] \qquad \text{(B.1-9)}$$

The use of expression (B.1-6) for B reduces the first term inside the brackets in equation (B.1-9) to

$$\frac{b}{2}\left(1 - B^{1/2}\right) = \frac{a}{2} \qquad \text{(B.1-10)}$$

For $|B|<1$, $\sin^{-1}(B)$ can be expanded as a power series [59], i.e.

$$\sin^{-1}(B) = B + \frac{1}{2}\frac{B^3}{3} + \frac{1\cdot 3}{2\cdot 4}\frac{B^5}{5} + \ldots \qquad \text{(B.1-11)}$$

Thus, the second term inside the brackets in equation (B.1-9) becomes

$$\frac{b}{2B}\sin^{-1}(B) = \frac{b}{2} + \frac{bB^2}{12} + \frac{3bB^4}{80} + \ldots \qquad \text{(B.1-12)}$$

Using equations (B-2) and (B.1-6) to evaluate powers of B, and neglecting terms of power e^2 and greater in equation (B.1-12) results in

$$\frac{b}{2B} \sin^{-1}(B) = (\frac{1}{2} + \frac{2}{3} e)a \qquad (B.1\text{-}13)$$

Finally, substituting eqautions (B.1-10) and (B.1-13) back into (B.1-9) yields an expression for the area in terms of 'a' and 'e', i.e.

$$A = 4\pi a^2 (1 + \frac{2}{3} e) \qquad (B.1\text{-}14)$$

B.2 Volume

The volume of the spheroid can be expressed as

$$V = 2 \int_0^b \pi r^2 dx \qquad (B.2\text{-}1)$$

where from equation (B-1),

$$r^2 = a^2 (1 - \frac{x^2}{b^2}) \qquad (B.2\text{-}2)$$

Using expression (B.2-2) in (B.2-1) results in

$$V = 2\pi a^2 \int_0^b (1 - \frac{x^2}{b^2}) \, dx \qquad (B.2\text{-}3)$$

Evaluating the integral in the equation above gives

$$V = \frac{4}{3} \pi a^2 b \qquad (B.2\text{-}4)$$

Substituting equation (B-2) for 'b' in equation (B.2-4) yields an expression for the volume in terms of 'a' and 'e', i.e.

$$V = \frac{4}{3} \pi a^3 (1 + e) \qquad \text{(B.2-5)}$$

B.3 Moment of Inertia

The moment of inertia for the spheroid about the axis of rotation can be expressed as

$$I = \rho^L \int_V r^2 \, DV \qquad \text{(B.3-1)}$$

where the density, ρ^L, is constant. The integral in equation (B.3-1) can be evaluated using cylindrical co-ordinates where 'x' corresponds to the cylinder axis, 'r' is the radial direction, and θ is the angle co-ordinate. The limits of integration for 'x' are obtained from equation (B-1) in terms of 'r', i.e.

$$x = \pm \frac{b}{a} (a^2 - r^2)^{1/2} \qquad \text{(B.3-2)}$$

For the volume element given by

$$DV = r \, dr \, d\theta \, dx \qquad \text{(B.3-3)}$$

expression (B.3-1) becomes

$$I = \rho^{L} \int_{-\frac{b}{a}(a^2-r^2)^{1/2}}^{\frac{b}{a}(a^2-r^2)^{1/2}} \int_{0}^{2\pi} \int_{0}^{a} r^3 dr\, d\theta\, dx \qquad \text{(B.3-4)}$$

Performing the integrations with respect to 'x' and θ in equation (B.3-4) gives

$$I = \frac{4\pi\rho^{L}b}{a} \int_{0}^{a} (a^2-r^2)^{1/2} r^3 \, dr \qquad \text{(B.3-5)}$$

Using integral tables [60] to perform the integration with respect to 'r' in equation (B.3-5) results in

$$I = \frac{4\pi\rho^{L}b}{a} \left[\frac{(a^2-r^2)^{5/2}}{5} - a^2 \frac{(a^2-r^2)^{3/2}}{3} \right]_{0}^{a} \qquad \text{(B.3-6)}$$

which reduces to

$$I = \frac{8\pi\rho^{L}ba^4}{15} \qquad \text{(B.3-7)}$$

Substituting equation (B-2) for 'b' in equation (B.3-7) yields an expression for the moment of inertia about the axis of rotation in terms of 'a' and 'e', i.e.

$$I = \frac{8\pi\rho^{L}(1 + e)a^{5}}{15} \qquad \text{(B.3-8)}$$

APPENDIX C

NUMERICAL DATA USED IN CALCULATIONS

C.1 Constants

Boltzmann's constant $k = 1.380 \times 10^{-23}$ J/°K

Avogadro's number $N_A = 6.023 \times 10^{26}$ $\frac{\text{molecules}}{\text{kg-mole}}$

C.2 Specific Volume, v^L [61]

Temperature (°C)	$v^L(H_2O)$ (m^3/kg)
0	0.001000
25	0.001003
50	0.001012
75	0.001026
100	0.001044
125	0.001065
150	0.001091
175	0.001121
200	0.001157
225	0.001199
250	0.001251
275	0.001317
300	0.001404

C.3 Vapor Pressure, P_v [62]

The values of the vapor pressure used in the calculations are presented in Table 2 for various temperatures. These values were obtained from the following equation for the vapor pressure as a function of the temperature, T, in degrees Kelvin:

$$P_v(\theta) = P_c \exp\left[\frac{1}{\theta}\,\frac{\sum_{n=1}^{5}(1-\theta)^n}{1+K_6(1-\theta)+K_7(1-\theta)^2} - \frac{1-\theta}{K_8(1-\theta)^2+K_9}\right] \qquad \text{(C.3-1)}$$

where $\theta \equiv \frac{T}{T_c}$

and the constants are as follows:

T_c = 647.3 °K

P_c = 22.120 MPa

K_1 = -7.6912

K_2 = -2.6080

K_3 = -1.6817

K_4 = 6.4233

K_5 = -1.1896

K_6 = 4.1671

K_7 = 2.0975

K_8 = 10^9

K_9 = 6

C.4 Partial Molar Volume, $\bar{V}_2$ [63]

The partial molar volume of air in water was approximated by the value of nitrogen in water at a temperature of 25°C, i.e.

$$\bar{V}_2 = 0.033 \text{ m}^3/\text{kg-mole}$$

Although rough correlations have been established for the temperature variation of the partial molar volume of a solute in a dilute solution [64], in view of the low level of accuracy involved, it was decided to use a constant value of $\bar{V}_2$ for all temperatures. It should be noted that equation (4-44) for 'h' is not highly sensitive to the value of $\bar{V}_2$. For example, at T = 25°C for P_c^L = -10 MPa and C = 10^{-4}, a fifty per cent increase in $\bar{V}_2$ changes the value of 'h' by less than half of one per cent.

C.5 Surface Tension, γ [65]

The values of the surface tension used in the calculations are presented in Table 2 for various temperatures. These values were obtained from the following equation for the surface tension of water in contact with its vapor as a function of the temperature, T, in degrees Kelvin:

$$\gamma(T) = 0.2358 \left(1 - \frac{T}{647.15}\right)^{1.256} \left[1 - 0.625\left(1 - \frac{T}{647.15}\right)\right] \text{ (N/m)} \qquad \text{(C.5-1)}$$

The effect of the dissolved gas on the surface tension was neglected. For a dilute solution, the reduction in the surface tension of the pure solvent can be expressed by

$$\Delta\gamma_o = \Gamma_2 RT \qquad (C.5\text{-}2)$$

where R is the gas constant, and Γ_2 is the adsorption of the solute at the interface [66]. For a dilute solution of nitrogen in water, the adsorption[1] was estimated to be of order 10^{-10}. Thus, since the adsorption is very small, the effect of the dissolved gas on the surface tension can be neglected.

C.6 Henry's Law Constant, K_H

The values of Henry's law constant used in the calculations are presented in Table 2 for various temperatures. For a dilute solution of air in water, K_H can be expressed in terms of K_{H2} and K_{H3} for dilute solutions of oxygen and nitrogen in water.

Consider a constant temperature, constant pressure system consisting of a dilute solution of air in water and an ideal gas mixture of air and water vapor. The liquid and gas subsystems, denoted by the superscripts L and G, are separated by a plane interface. The argon free air in the gas-vapor mixture is assumed to consist of twenty-one per

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[1] See footnote 6 in Section 2.2.

cent oxygen and seventy-nine per cent nitrogen. The water, oxygen, and nitrogen are denoted by the subscripts 1, 2, and 3, respectively.

Setting the variation of the Gibbs potential equal to zero for constant temperature, T, pressure, P, and total mole numbers, N_i, yields the equilibrium conditions, i.e.

$$\mu_i^L = \mu_i^G \qquad i = 1,2,3 \qquad \text{(C.6-1)}$$

Using the expressions for the chemical potentials of the gas components in the dilute solution and ideal gas mixture in equation (C.6-1) gives

$$\mu_{0i}^G (P_r,T) + kT \ln \left(\frac{PX_i}{P_r}\right)$$

$$= \psi(P,T) + kT \ln C_i \qquad i=2,3 \qquad \text{(C.6-2)}$$

Let the reference system for each gas be the liquid saturated with the gas across a non-rigid membrane, permeable only to the gas component. If C_{i_o} is the saturation concentration of component i, the equality of chemical potentials across the membrane gives

$$\psi(P,T) - \mu_{0i}^G (P,T) = kT \ln \left(\frac{1}{C_{i_o}}\right) \qquad i=2,3 \qquad \text{(C.6-3)}$$

Substituting equation (C.6-3) back into (C.6-2) and choosing the reference pressure, P_r, to be equal to P results in

$$PX_2 = K_{H2}\, C_2 \qquad \text{(C.6-4)}$$

and

$$PX_3 = K_{H3}\, C_3 \qquad \text{(C.6-5)}$$

where Henry's law constant, K_{Hi}, for each gas component is given by

$$K_{Hi} \equiv \frac{P}{C_{i_o}} \qquad i=2,3 \qquad \text{(C.6-6)}$$

Dividing equation (C.6-4) by (C.6-5) and rearranging gives

$$C_2 = q\, C_3 \qquad \text{(C.6-7)}$$

where

$$q \equiv \frac{X_2}{X_3}\,\frac{K_{H3}}{K_{H2}} \qquad \text{(C.6-8)}$$

For the air in the gas-vapor mixture, the ratio of the mole fraction of oxygen to nitrogen is fixed, i.e.

$$\frac{X_2}{X_3} = \frac{0.21}{0.79} \cong 0.266 \qquad \text{(C.6-9)}$$

Thus, expression (C.6-8) for q becomes

$$q = 0.266\,\frac{K_{H3}}{K_{H2}} \qquad \text{(C.6-10)}$$

If K_H is Henry's law constant for a dilute solution of air in water treating air as a single component, then

$$P(X_2 + X_3) = K_H (C_1 + C_2) \qquad \text{(C.6-11)}$$

Adding equations (C.6-4) and (C.6-5) gives

$$P(X_2 + X_3) = K_{H2}C_2 + K_{H3}C_3 \qquad \text{(C.6-12)}$$

From equations (C.6-11) and (C.6-12),

$$K_H (C_1 + C_2) = K_{H2}C_2 + K_{H3}C_3 \qquad \text{(C.6-13)}$$

Substituting equations (C.6-7) and (C.6-10) into (C.6-13) and rearranging results in

$$K_H = \frac{1.266 \; K_{H3}}{\left(1 + 0.266 \frac{K_{H3}}{K_{H2}}\right)} \qquad \text{(C.6-14)}$$

Equation (C.6-14) expresses K_H for a dilute solution of air in water in terms of K_{H2} and K_{H3} for dilute solutions of oxygen and nitrogen in water, respectively.

The values of K_{H2} and K_{H3} [67] were obtained from the following equation for Henry's law constant as a function of the temperature, T, in degrees Kelvin:

$$K_H(T_1) = (1.013 \times 10^3) \exp \left[- \frac{(CT_1 + D)}{2A} + \right.$$

$$\left. + \frac{1}{2A} \sqrt{(CT_1 + D)^2 - 4A (BT_1^2 + ET_1 - 1)} \right] \quad \text{(MPa)}$$

$$\text{(C.6-15)}$$

where

$$T_1 = \frac{10^3}{T}$$

and the values of the constants A, B, C, D, and E are given as follows for oxygen and nitrogen:

oxygen		nitrogen	
A =	-0.0005943	A =	-0.1021
B =	-0.1470	B =	-0.1482
C =	-0.05120	C =	-0.01900
D =	-0.1076	D =	-0.03741
E =	0.8447	E =	0.8510